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Über den Gleichgewichtszustand Gemischter Salzlösung.

Von

Nobuji Sasaki.

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In der vorliegenden Abhandlung beabsichtige ich, den Gleichgewichtszustand einer aus zwei einwertigen gleichartigen Anionen und mehreren Kationen von verschiedener Wertigkeit bestehenden gemischten Lözung mathematisch unterzusuchen.

Als Beispiel denken wir uns eine Lösung, welche eine bestimmte Menge von Ferrichlorid, Bromnatrium, Chlornatrium und Salzsäure enthält. Im Gleichgewichte gibt es in der Lösung folgende Ionen und Ionengruppen :

1. Freie Ionen : $Na^{\cdot}$, $H^{\cdot}$, $Fe^{\cdot\cdot\cdot}$, Cl', Br';
   Anzahl b_0 c_0 d_0 a_1 a_2 $a_1+a_2=a$;
2. Ionengruppen von dem Typus NaX :
   NaCl, NaBr ;
   Anzahl b_1 b_2 $b_1+b_2=b$;
3. Ionengruppen von dem Typus HX :
   HCl, HBr ;
   Anzahl c_1 c_2 $c_1+c_2=c$;
4. Ionengruppen von dem Typus $FeX^{\cdot\cdot}$:
   $FeCl^{\cdot\cdot}$, $FeBr^{\cdot\cdot}$;
   Anzahl d_1 d_2 $d_1+d_2=d$;

5. Ionengruppen von dem Typus FeX'_2:

$$FeCl'_2, \quad FeClBr', \quad FeBr'_2;$$

Anzahl e_1 e_2 e_3 $e_1+e_2+e_3=e$;

6. Ionengruppen von dem Typus FeX_3:

$$FeCl_3, \quad FeCl_2Br, \quad FeClBr_2, \quad FeBr_3;$$

Anzahl f_1 f_2 f_3 f_4 $f_1+f_2+f_3+f_4=f$.

Wir wollen hier annehmen, dass sowohl Chlor- als auch Bromion elektrolytisch ein identisches Verhalten haben. Unter dieser Annahme sind die Grössen b_0, c_0, d_0, a, b, c, d, e und f durch die zugesetzten Mengen von Ferrichlorid, Bromnatrium, Chlornatrium und Salzsäure eindeutig bestimmt. Indem man daher die genannten Grössen als bekannt ansieht, wollen wir die Grössen a_1, a_2, b_1, b_2, c_1, c_2, d_1, d_2, e_1, e_2, e_3, f_1, f_2, f_3 und f_4 nach statistischer Methode berechnen.

Ist die Gesamtanzahl von Chlorion in der Lösung m, und die von Bromion n, so gelten die Beziehungen:

$$\left.\begin{aligned} m&=a_1+b_1+c_1+d_1+2e_1+e_2+3f_1+2f_2+f_3 \\ n&=a_2+b_2+c_2+d_2+e_2+2e_3+f_2+2f_3+3f_4 \end{aligned}\right\} \qquad (1)$$

$$\left.\begin{aligned} a_1+a_2&=a, \\ b_1+b_2&=b, \\ c_1+c_2&=c, \\ d_1+d_2&=d, \\ e_1+e_2+e_3&=e, \\ f_1+f_2+f_3+f_4&=f. \end{aligned}\right\} \qquad (2)$$

Von den zwei Beziehungen (1) ist nur eine unabhängig, weil die andere aus den übrigen abgeleitet werden kann.

Wir wollen zunächst berechnen, in wieviel verschiedenen Weisen die angegebene Chlor-Bromionenverteilung aus m Chlor- und n Bromionen gewonnen werden kann. Aus m Chlorionen kann man z. B. auf

$$\frac{mPa_1}{(1!)^{a_1}} \cdot \frac{1}{a_1!}$$

verschiedene Weisen a_1 Chlorionen auswählen, und aus den gebliebenen

$m-a_1$ Chlorionen auf

$$\frac{(m-a_1)Pb_1}{(1!)^{b_1}} \cdot \frac{1}{b_1!}$$

verschiedene Weisen b_1 Chlorionen auswählen, usw. Unten werden auf diese Weise berechnete Anzahl der Auswählungsweisen für einzelne Ionengruppen gegeben.

Cl' a_1	$\frac{mPa_1}{(1!)^{a_1}} \cdot \frac{1}{a_1!}$	Br' a_2	$\frac{nPa_2}{(1!)^{a_2}} \cdot \frac{1}{a_2!}$
$NaCl$ b_1	$\frac{(m-a_1)Pb_1}{(1!)^{b_1}} \cdot \frac{1}{b_1!}$	$NaBr$ b_2	$\frac{(n-a_2)Pb_2}{(1!)^{b_2}} \cdot \frac{1}{b_2!}$
HCl c_1	$\frac{(m-a_1-b_1)Pc_1}{(1!)^{c_1}} \cdot \frac{1}{c_1!}$	HBr c_2	$\frac{(n-a_2-b_2)Pc_2}{(1!)^{c_2}} \cdot \frac{1}{c_2!}$
$FeCl''$ d_1	$\frac{(m-a_1-b_1-c_1)Pd_1}{(1!)^{d_1}} \cdot \frac{1}{d_1!}$	$FeBr''$ d_2	$\frac{(n-a_2-b_2-c_2)Pd_2}{(1!)^{d_2}} \cdot \frac{1}{d_2!}$
$FeCl'_2$ e_1	$\frac{(m-a_1-b_1-c_1-d_1)P2e_1}{(2!)^{e_1}} \cdot \frac{1}{e_1!}$		
$FeClBr'$ e_2	$\frac{(m-a_1-b_1-c_1-d_1-2e_1)Pe_2}{(1!)^{e_2}} \cdot \frac{(n-a_2-b_2-c_2-d_2)Pe_2}{(1!)^{e_2}} \cdot \frac{1}{e_2!}$		
$FeBr'_2$ e_3	$\frac{(n-a_2-b_2-c_2-d_2-e_2)P2e_3}{(2!)^{e_3}} \cdot \frac{1}{e_3!}$		
$FeCl_3$ f_1	$\frac{(m-a_1-b_1-c_1-d_1-2e_1-e_2)P3f_1}{(3!)^{f_1}} \cdot \frac{1}{f_1!}$		
$FeCl_2Br$ f_2	$\frac{(m-a_1-b_1-c_1-d_1-2e_1-c_2-3f_1)P2f_2}{(2!)^{f_2}} \cdot \frac{(n-a_2-b_2-c_2-d_2-e_2-2e_3)Pf_2}{(1!)^{f_2}} \cdot \frac{1}{f_2!}$		

$$\left.\begin{array}{l} \underset{f_3}{\mathrm{FeClBr_2}} \quad \dfrac{(m-a_1-b_1-c_1-d_1-2e_1-e_2-3f_1-2f_2)Pf_3}{(1!)^{f_3}} \\ \qquad\qquad \dfrac{(n-a_2-b_2-c_2-d_2-e_2-2e_3-f_2)P2f_3}{(2!)^{f_3}} \cdot \dfrac{1}{f_3!} \end{array}\right\}$$

$$\underset{f_4}{\mathrm{FeBr_3}} \quad \frac{(n-a_2-b_2-c_2-d_2-e_2-2e_3-f_2-2f_3)P3f_4}{(3!)^{f_4}} \cdot \frac{1}{f_4!}$$

Das Produkt aus allen diesen Zahlen θ gibt die gesuchte Anzahl der verschiedenen Zusammensetzungsweisen der oben gegebenen Ionenverteilung an:

$$\theta = \frac{m!\, n!}{a_1!\, a_2!\, b_1!\, b_2!\, c_1!\, c_2!\, d_1!\, d_2!\, e_1!\, e_2!\, e_3!\, f_1!\, f_2!\, f_3!\, f_4!\; 2^{e_1} 2^{e_3} 3^{f_1} 3^{f_4} 2^{f}} .$$

Da a_1, a_2, usw. alle sehr gross sind, so kann man hier die Stirlingsche Formel

$$n! = \sqrt{2\pi n}\, n^n e^{-n}$$

anwenden. Durch Einsetzung der Formel erhält man

$$\theta = \frac{A}{K},$$

wobei

$$A = \frac{m!\, n!\, e^{a+b+c+d+e+f}}{(\sqrt{2\pi})^{15}\; 2^{f}},$$

$$\left.\begin{array}{l} K = a_1^{a_1+\frac{1}{2}} a_2^{a_2+\frac{1}{2}} b_1^{b_1+\frac{1}{2}} b_2^{b_2+\frac{1}{2}} c_1^{c_1+\frac{1}{2}} c_2^{c_2+\frac{1}{2}} d_1^{d_1+\frac{1}{2}} d_2^{d_2+\frac{1}{2}} e_1^{e_1+\frac{1}{2}} \\ \qquad 2^{e_1} e_2^{e_2+\frac{1}{2}} e_3^{e_3+\frac{1}{2}} 2^{e_3} f_1^{f_1+\frac{1}{2}} 3^{f_1} f_2^{f_2+\frac{1}{2}} f_3^{f_3+\frac{1}{2}} f_4^{f_4+\frac{1}{2}} 3^{f_4}. \end{array}\right\}$$

Wir wollen hier annehmen, dass im Gleichgewichte die wirkliche Ionenverteilung diejenige sein soll, welche die höchste Wahrscheinlichkeit hat, d. h. diejenige, welche den grössten Wert von θ hat. θ ist maximal, wenn K minimal ist. Man gewinnt als die Maximum- bezw. Minimumbedingung

$$\frac{\delta K}{K}=\left(\log a_1+1+\frac{1}{2a_1}\right)\delta a_1+\left(\log a_2+1+\frac{1}{2a_2}\right)\delta a_2+\ldots\ldots$$

$$+\left(\log d_2+1+\frac{1}{2d_2}\right)\delta d_2+\left(\log 2e_1+1+\frac{1}{2e_1}\right)\delta e_1+\left(\log e_2+1+\frac{1}{2e_2}\right)\delta e_2$$

$$+\left(\log 2e_3+1+\frac{1}{2e_3}\right)\delta e_3+\left(\log 3f_1+1+\frac{1}{2f_1}\right)\delta f_1+\left(\log f_2+1+\frac{1}{2f_2}\right)\delta f_2$$

$$+\left(\lg f_3+1+\frac{1}{2f_3}\right)\delta f_3+\left(\log 3f_4+1+\frac{1}{2f_4}\right)\delta f_4=0.$$

Andererseits erhält man aus Bedingung (2)

$$\delta a_2=-\delta a_1,\ \delta b_2=-\delta b_1,\ \delta c_2=-\delta c_1,\ \delta d_2=-\delta d_1,$$
$$\delta e_2=-\delta e_1-\delta e_3,\ \delta f_3=-\delta f_1-\delta f_2-\delta f_4.$$

Durch Einsetzung dieser Beziehungen und Vernachlässigung von der sehr kleinen Grösse $1/2a_1$ gegen $\log a_1+1$ usw. erhält man

$$\left.\begin{aligned}\frac{\delta K}{K}&=\log\frac{a_1}{a_2}\delta a_1+\ldots.+\log\frac{d_1}{d_2}\delta d_1+\log\frac{2e_1}{e_2}\delta e_1+\log\frac{2e_3}{e_2}\delta e_3\\&+\log\frac{3f_1}{f_3}\delta f_1+\log\frac{f_2}{f_3}\delta f_2+\log\frac{3f_4}{f_3}\delta f_4=0.\end{aligned}\right\}\quad(3)$$

Aus Bedingung (1) folgt

$$\delta a_1+\delta b_1+\delta c_1+\delta d_1+2\delta e_1+\delta e_2+3\delta f_1+2\delta f_2+\delta f_3=0\ ;$$

aus Bedingung (2) folgt

$$\delta e_1+\delta e_2+\delta e_3=0,$$
$$\delta f_1+\delta f_2+\delta f_3+\delta f_4=0.$$

Durch Subtrahieren der letzten zwei Gleichungen von der ersten haben wir

$$\delta a_1+\delta b_1+\delta c_1+\delta d_1+\delta e_1-\delta e_3+2\delta f_1+\delta f_2-\delta f_4=0.\qquad(4)$$

Multipliziert man (4) mit λ, einem unbestimmten Multiplikator und addiert dann zu (3), so erhält man

$$\left.\frac{\delta K}{K}=\left(\log\frac{a_1}{a_2}+\lambda\right)\delta a_1+\ldots.+\left(\log\frac{d_1}{d_2}+\lambda\right)\delta d_1+\left(\log\frac{2e_1}{e_2}+\lambda\right)\delta e_1\right|$$

$$+\left(\log\frac{2e_3}{e_2}-\lambda\right)\delta e_3+\left(\log\frac{3f_1}{f_3}+2\lambda\right)\delta f_1+\left(\log\frac{f_2}{f_3}+\lambda\right)\delta f_2$$
$$+\left(\log\frac{3f_4}{f_3}-\lambda\right)\delta f_4=0,$$

woraus folgt

$$\log\frac{a_1}{a_2}+\lambda=0,\ \log\frac{b_1}{b_2}+\lambda=0,\ \log\frac{c_1}{c_2}+\lambda=0,\ \log\frac{d_1}{d_2}+\lambda=0, \qquad (5_1)$$

$$\log\frac{2e_1}{e_2}+\lambda=0,\ \log\frac{2e_3}{e_2}-\lambda=0, \qquad (5_2)$$

$$\log\frac{3f_1}{f_3}+2\lambda=0,\ \log\frac{f_2}{f_3}+\lambda=0,\ \log\frac{3f_4}{f_3}-\lambda=0. \qquad (5_3)$$

Die Gleichungen (5_1) und (5_2) und die letzten zwei von (5_3) geben

$$e^{-\lambda}=\frac{a_1}{a_2}=\frac{b_1}{b_2}=\frac{c_1}{c_2}=\frac{d_1}{d_2}=\frac{2e_1}{e_2}=\frac{e_2}{2e_3}=\frac{f_2}{f_3}=\frac{f_3}{3f_4}. \qquad (6)$$

Die ersten zwei von (5_3) geben

$$\frac{3f_1}{f_3}=\frac{f_2^2}{f_3^2},$$

woraus folgt

$$\frac{3f_1}{f_2}=\frac{f_2}{f_3}.$$

Also haben wir

$$e^{-\lambda}=\frac{a_1}{a_2}=\frac{b_1}{b_2}=\frac{c_1}{c_2}=\frac{d_1}{d_2}=\frac{2e_1}{e_2}=\frac{e_2}{2e_3}=\frac{3f_1}{f_2}=\frac{f_2}{f_3}=\frac{f_3}{3f_4},$$

aus welcher Gleichung folgt

$$e^{-\lambda}=\frac{a_1+b_1+c_1+d_1+2e_1+e_2+3f_1+2f_2+f_3}{a_2+b_2+c_2+d_2+e_2+2e_3+f_2+2f_3+3f_4}.$$

Daher ist $e^{-\lambda}$ gemäss (1) gleich $\frac{m}{n}$.

Schliesslich haben wir

$$\frac{m}{n}=\frac{a_1}{a_2}=\frac{b_1}{b_2}=\frac{c_1}{c_2}=\frac{d_1}{d_2}=\frac{2e_1}{e_2}=\frac{e_2}{2e_3}=\frac{3f_1}{f_2}=\frac{f_2}{f_3}=\frac{f_3}{3f_4}. \qquad (7)$$

Aus Gleichungen (2) und (7) ergibt sich die Anzahl der Ionengruppen:

$$a_1=\frac{m}{m+n}a, \qquad a_2=\frac{n}{m+n}a,$$

$$b_1=\frac{m}{m+n}b, \qquad b_2=\frac{n}{m+n}b,$$

$$c_1=\frac{m}{m+n}c, \qquad c_2=\frac{n}{m+n}c,$$

$$d_1=\frac{m}{m+n}d, \qquad d_2=\frac{n}{m+n}d,$$

$$e_1=\frac{m^2}{(m+n)^2}e, \qquad e_2=\frac{2mn}{(m+n)^2}e, \qquad e_3=\frac{n^2}{(m+n)^2}e,$$

$$f_1=\frac{m^3}{(m+n)^3}f, \quad f_2=\frac{3m^2n}{(m+n)^3}f, \quad f_3=\frac{3mn^2}{(m+n)^3}f, \quad f_4=\frac{n^3}{(m+n)^3}f.$$

Dass diese Verteilung von Chlor- und Bromionen die höchste Wahrscheinlichkeit besitzt, kann folgenderweise bewiesen werden. Wie oben erhalten, ist

$$\delta K=K\left[\left(\log a_1+1+\frac{1}{2a_1}\right)\delta a_1+\ldots\ldots+\left(\log 3f_4+1+\frac{1}{2f_4}\right)\delta f_4\right].$$

Folglich ist

$$\delta^2K=\frac{(\delta K)^2}{K}+K\left[\left(\frac{1}{a_1}-\frac{1}{2a_1^2}\right)\left(\delta a_1\right)^2+\ldots\ldots+\left(\frac{1}{f_4}-\frac{1}{2f_4^2}\right)\left(\delta f_4\right)^2\right],$$

woraus man gleich ersiht, dass δ^2K stets positiv ist. Also ist K minimal und θ deshalb maximal für die erhaltenen Werte der Ionengruppen. Diese Ionenverteilung ist sonach die wahrscheinlichste.

Zusammenfassung.

Es wurden am Beispiel der gemischten Lösung von $FeCl_3$, NaCl, HCl und NaBr die Konzentrationen aller möglichen Ionen and Ionengruppen nach statistischer Methode berechenet.

Es ist mir eine angenehme Pflicht, meinem hochverehrten Lehrer Herrn Prof. Dr. M. Chikashige für seine ständige Unterstützung und auch Herrn Prof. Dr. M. Sono für seine freundliche Durchsicht an dieser Stelle meinen herzlichsten Dank auszusprechen.

Über die Dissoziation Mehratomiger Salze.

Von

Nobuji Sasaki.

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In der vorliegenden Abhandlung soll die Abhängigkeit des Dissoziationszustandes eines mehratomigen Salzes von der Gesamt–, von der Kationen– und von der Anionenkonzentration mathematisch untersucht werden.

Als Beispiel nehmen wir Ferrichlorid, welches in folgender Schema dissoziiert :

$$\begin{aligned} Fe^{\cdots} &+ Cl' \rightleftharpoons FeCl^{\cdot\cdot}, \\ FeCl^{\cdot\cdot} &+ Cl' \rightleftharpoons FeCl^{\cdot}_2, \\ FeCl^{\cdot}_2 &+ Cl' \rightleftharpoons FeCl_3. \end{aligned}$$

Setzt man zu dieser Lösung eine Gemenge d' von Ferrichlorid hinzu, so wird der Gleichgewichtszustand zerstört und ein neuer sich einstellen. Die Konzentrationen der Ionen ($FeCl_3$ einschliessend) vor und nach dem Zusatz von Ferrichlorid wollen wir durch folgende Tabelle bezeichnen :

	Vor dem Zusatz	Nach dem Zusatz
$Fe^{\cdots}$	a	$a+x$
$FeCl^{\cdot\cdot}$	b	$b+y$
$FeCl^{\cdot}_2$	c	$c+z$
$FeCl_3$	d	$d+d'-x-y-z$
Cl'	e	$e+3x+2y+z$,

wobei offenbar

$$e = 3a+2b+c.$$

Die Gleichgewichtsgleichungen sind demnach vor dem Zusatz

$$ae = K_1 b,$$
$$be = K_2 c,$$
$$ce = K_3 d,$$

und nach dem Zusatz

$$(a+x)(e+3x+2y+z) = K_1(b+y),$$
$$(b+y)(e+3x+2y+z) = K_2(c+z),$$
$$(c+z)(e+3x+2y+z) = K_3(d+d'-x-y-z),$$

wodei K_1 usw. die Gleichgewichtskonstanten der einzelnen Reaktionen bezeichnen.

Falls die zugesetzte Ferrichloridmenge d' sehr klein ist, so sind x,y und z auch sehr klein. Die letzten drei Gleichungen können dann folgenderweise vereinfacht werden:

$$\frac{x}{a}+\frac{3x+2y+z}{e}-\frac{y}{b}=0,$$

$$\frac{y}{b}+\frac{3x+2y+z}{e}-\frac{z}{c}=0,$$

$$\frac{z}{c}+\frac{3x+2y+z}{e}-\frac{d'-x-y-z}{d}=0.$$

Aus diesen drei Gleichungen erhält man

$$x=\frac{d'}{d}\cdot\frac{e-2(b+c)}{bce}\cdot\frac{1}{\Delta}=\frac{d'}{d}\cdot\frac{3a-c}{bce}\cdot\frac{1}{\Delta},$$

$$y=\frac{d'}{d}\cdot\frac{3a+e-c}{ace}\cdot\frac{1}{\Delta}=\frac{d'}{d}\cdot\frac{6a+2b}{ace}\cdot\frac{1}{\Delta},$$

$$z=\frac{d'}{d}\cdot\frac{6a+2b+e}{abe}\cdot\frac{1}{\Delta},$$

wobei $\Delta=\{a(b+4c+9d)+b(c+4d)+cd+e(a+b+c+d)\}/abcde.$

Man erhält daraus noch

$$3x+2y+z=\frac{d'}{d}\cdot\frac{3a+2b+c}{abc}\cdot\frac{1}{\Delta},$$

$$p'-x-y-z=\frac{dz}{c}+\frac{d'(3a+2b+c)}{abce}\cdot\frac{1}{\Delta}.$$

Da, wie ersichtlich, y, z, $3x+2y+z$ und $d'-x-y-z$ alle positiv sind, so ist es klar, dass $FeCl^{\cdot\cdot}$, $FeCl^{\cdot}_2$, $FeCl_3$ und Cl' alle stets zunehmen müssen, wenn die Ferrichloridlösung in ihrer Konzentration zunimmt. Was $Fe^{\cdot\cdot\cdot}$ betrifft, so ist

$$x \gtreqless 0, \text{ je nachdem } 3a-c \gtreqless 0 \text{ ist.}$$

Bezeichnet man die Ionenkonzentrationen nach dem Zusatz von d' Ferrichlorid mit αa, βb, γc, δd und εe, so erhält man leicht die Beziehung:

$$\alpha : \beta : \gamma : \delta = 1 : \varepsilon : \varepsilon^2 : \varepsilon^3.$$

Im vorliegenden Falle ist $\varepsilon > 1$, da $3x+2y+z > 0$ ist. Wird also die Ferrichloridlösung konzentrierter, so werden die komplexeren Ionen viel schneller in ihrer Konzentration zunehmen als die weniger komplexeren und umgekehrt. Aus dieser Erwägung ist ersichtlich, dass die Beziehungen $3a-c >, =, < 0$ im Verlaufe der Konzentrationszunahme der Reihe nach befriedigt werden. $Fe^{\cdot\cdot\cdot}$ wird also beim ständigen Zusatz von Ferrichlorid zum reinen Wasser anfänglich zunehmen ($3a-c>0$) und dann eine maximale Konzentration erreichen ($3a-c=0$), um dann abzunehmen zu beginnen ($3a-c<0$).

Im nächsten Falle wollen wir das Ferriion allein von der Lösung wegnehmen und dessen Einfluss studieren. Wegnahme des Ferriions allein geschieht derart, dass man von der Lösung das Ferrichlorid wegnimmt und durch Zusatz einer entsprechenden Menge Chlornatrium den Verlust an Chlorion kompensiert. Chlornatrium wird hierbei als vollständig dissoziierbar angenommen.

Die Konzentrationen der Ionen vor und nach der Wegnahme der a' Menge von $Fe^{\cdot\cdot\cdot}$ sind:

	Vor der Wegnahme	Nach der Wegnahme
$Fe^{\cdot\cdot\cdot}$	a	$a+x+y+z-a'$
$FeCl^{\cdot\cdot}$	b	$b-x$
$FeCl^{\cdot}_2$	c	$c-y$
$FeCl_3$	d	$d-z$
Cl'	$e+e'$	$e+e'+x+2y+3z$,

wobei e' eine vorher im Überschuss zugesetzte Chlorionenmenge bezeichnet.

Ist a' sehr klein, so kann man die Gleichgewichtsbedingungen folgenderweise schreiben:

$$\frac{x+y+z-a'}{a}+\frac{x+2y+3z}{e+e'}+\frac{x}{b}=0,$$

$$-\frac{x}{b}+\frac{x+2y+3z}{e+e'}+\frac{y}{c}=0,$$

$$-\frac{y}{c}+\frac{x+2y+3z}{e+e'}+\frac{z}{d}=0,$$

woraus man erhält

$$x=\frac{a'}{a}\cdot\frac{2c+6d+e+e'}{cd(e+e')}\cdot\frac{1}{\Delta},$$

$$y=\frac{a'}{a}\cdot\frac{-b+3d+e+e'}{bd(e+e')}\cdot\frac{1}{\Delta}=\frac{a'}{a}\cdot\frac{3a+b+c+3d+e'}{bd(e+e')}\cdot\frac{1}{\Delta},$$

$$z=\frac{a'}{a}\cdot\frac{e+e'-2b-2c}{bc(e+e')}\cdot\frac{1}{\Delta}=\frac{a'}{a}\cdot\frac{3a-c+e'}{bc(e+e')}\cdot\frac{1}{\Delta},$$

wobei Δ gleich wie im vorigen Falle ist, e muss aber hier in $e+e'$ umgeschrieben werden.

Man erhält ferner

$$x+2y+3z=\frac{a'}{a}\cdot\frac{b+2c+3d}{bcd}\cdot\frac{1}{\Delta},$$

$$x+y+z-a'=-\frac{ax}{b}-\frac{a'(b+2c+3d)}{bcd(e+e')}\cdot\frac{1}{\Delta}.$$

Da, wie ersichtlich, x, y, und $x+2y+3z$ alle positiv und $x+y+z-a'$ negativ ist, so folgt, dass durch Wegnahme des Ferriions $Fe^{\cdots}$, $FeCl^{\cdot\cdot}$ und $FeCl^{\cdot}_2$ stets abnehmen, während Cl' stets zunimmt. Was $FeCl_3$ betrifft, so ist

$$z\gtreqless 0, \quad \text{je nachdem} \quad 3a+e'-c\gtreqless 0 \quad \text{ist.}$$

Durch Wegnahme des Ferriions nimmt also $FeCl_3$ bei hoher Konzentration zu; da aber e' bei fortwährender Wegnahme des Ferriions

zunimmt, so muss bald $3a+e'-c \gtrless 0$ werden, d. h. $FeCl_3$ hierbei abzunehmen beginnen. Bei niedriger Konzentration oder in Gegenwart von genügend grossem Überschuss von Chlorion nimmt $FeCl_3$ stets ab. Diese notwendige überschüssige Chlorionenmenge übertrifft schon die hinreichende, wenn sie einem Drittel der der Ferriionenmenge entsprechenden Chlorionenmenge gleich, d. h. $e'=a+b+c+d$ ist, wobei $3a+e'-c=4a+b+d$ offenbar immer positiv ist.

Schliesslich wollen wir den Einfluss von Zusatz des Chlorions allein studieren. Die Konzentration der Ionen vor und nach dem Chlorionzusatz e' sind:

	Vor dem Zusatz	Nach dem Zusatz
$Fe^{\cdots}$	a	$a-x-y-z$
$FeCl^{\cdot\cdot}$	b	$b+x$
$FeCl^{\cdot}_2$	c	$c+y$
$FeCl_3$	d	$d+z$
Cl'	e	$e+e'-x-2y-3z$,

wobei $e=3a+2b+c+e''$ ist, (e'': die vorher überschüssig enthaltene Chlorionenmenge).

Falls e' sehr klein ist, so erhält man ähnlicherweise folgende drei Gleichungen:

$$\frac{-x-y-z}{a}+\frac{e'-x-2y-3z}{e}-\frac{x}{b}=0,$$

$$\frac{x}{b}+\frac{e'-x-2y-3z}{e}-\frac{y}{c}=0,$$

$$\frac{y}{c}+\frac{e'-x-2y-3z}{e}-\frac{z}{d}=0,$$

woraus man erhält

$$x=\frac{e'}{e}\cdot\frac{a-c-2d}{acd}\cdot\frac{1}{\Delta},$$

$$y=\frac{e'}{e}\cdot\frac{2a+b-d}{abd}\cdot\frac{1}{\Delta},$$

$$z=\frac{e'}{e}\cdot\frac{3a+2b+c}{abc}\cdot\frac{1}{\Delta},$$

wobei Δ gleich wie oben ist.
Ferner gewinnt man

$$x+y+z=\frac{e'}{e}\cdot\frac{b+2c+3d}{bcd}\cdot\frac{1}{\Delta},$$

$$e'-x-2y-3z=\frac{e'(a+b+c+d)}{abcd}\cdot\frac{1}{\Delta}.$$

Da, wie ersichtlich, z, $e'-x-2y-3z$ und $x+y+z$ positiv sind, so nehmen durch Chlorionzusatz $FeCl_3$ und Cl' stets zu und Fe''' ab. Was $FeCl''$ und $FeCl'_2$ betrifft, so haben wir

$x \gtreqless 0$, je nachdem $a-c-2d \gtreqless 0$,
und $y \gtreqless 0$, je nachdem $2a+b-d \gtreqless 0$ ist.

Da $2a+b-d=(a-c-2d)+(a+b+c+d)$ ist, so bleibt die Beziehung $2a+b-d>0$ bestehen sofern als $a-c-2d>0$, $=0$ und noch etwas weiter. Wie oben gesehen, haben wir die Beziehung

$$\alpha:\beta:\gamma:\delta = 1:\varepsilon:\varepsilon^2:\varepsilon^3$$

und da $\varepsilon>1$ ist, so werden c und d bei fortwährendem Chlorionzusatz vor a und b vorzuherrschen beginnen

Wir nehmen an, dass die anfängliche Ferrichloridlösung so verdünnt ist, dass die Bedingung $a-c-2d>0$ bestehen kann. Setzt man zur Lösung ständigerweise Chlorion hinzu, so wird zu Anfang Fe''' ab- und $FeCl''$, $FeCl'_2$ und $FeCl_3$ zunehmen. Aber bald wird ein Punkt kommen, wobei $a-c-2d=0$ wird. Von diesem Punkt an beginnt $FeCl''$ abzunehmen, während $FeCl'_2$ und $FeCl_3$ noch ihre Zunahme fortsetzen, bis $2a+b-d=0$ wird. Von da ab nehmen sowohl $FeCl''$ als auch $FeCl'_2$ ab, bis schliesslich fast alle Ferriionen in $FeCl_3$ übergegangen sind.

Im folgenden wollen wir die Konzentrationsänderung der Ionen durch Chlorionzusatz etwas quantitativer behandeln.

Durch Zusatz von vollständig dissoziierendem Chlorsalz sei die Chlorionenmenge ver-p-facht. Ergänzt man die dadurch herbeigeführte Verminderung von freiem Ferriion (siehe oben) durch Zusatz

desselben, so erhält man folgende Beziehung:

$$\alpha=1$$

und deshalb $$\beta=\varepsilon,\ \gamma=\varepsilon^2,\ \delta=\varepsilon^3.$$

Betreffs der Chlorionenmenge besteht die Gleichung

$$(e+b+2c+3d)p=(e+b+2\varepsilon c+3\varepsilon^2 d)\varepsilon.$$

Da aber $\varepsilon>1$ ist, so muss

$$\varepsilon<p$$

sein. Daraus folgt

$$\beta<p,\quad \gamma<p^2,\quad \delta<p^3.$$

Entzieht man nun der Lösung die nachher zugesetzte Menge Ferriion, so werden β und γ abnehmen und auch so δ, vorausgesetzt, dass die Beziehung $3a+e'-c>0$ besteht (siehe oben). Ver-p-facht man also die Chlorionenmenge, so erhalten wir die Beziehungen

$$\beta<p,\quad \gamma<p^2,\quad \delta<p^3,$$

vorausgesetzt, dass die Lösung eine genügend überschüssige Chlorionenmenge enthält.

Ist die Lösung sehr verdünnt und das Ferrichlorid fast vollständig dissoziiert ist (ohne Hydrolyse), so wird

$$\varepsilon\doteq p,$$

vorausgesetzt, dass $p-1$ sehr klein ist, denn dann b, βb, c, γc, d und δd können gegen a und e vernachlässigt werden. In diesem Grenzfalle erhält man also

$$\beta\doteq p,\ \gamma\doteq p^2,\ \delta\doteq p^3.$$

Falls andererseits die Lösung sehr konzentriert ist oder einen sehr grossen Überschuss von Chlorion enthält, so wird δ fast gleich eins, denn $FeCl_3$ kann nunmehr durch Zusatz von Chlorion nur sehr wenig zunehmen. β und γ werden, wie oben erwähnt, von einem Punkt an durch Zusatz von Chlorion abnehmen. Man dürfte also folgende Grenzen von β, γ und δ als geltend ansehen:

$$0<\beta<p,\quad 0<\gamma<p^2,\quad 1<\delta<p^3.$$

Eine nähere quantitative Beziehung wäre schwer zu erhalten.

Zusammenfassung.

Es wurde am Beispiel von Ferrichloridlösung mathematisch untersucht, wie die Konzentration des Moleküls und seiner Dissoziationsprodukte aller Stufen von der Gesamt–, von der Kationen– und von der Anionenkonzentration abhängen.

Es ist mir eine angenehme Pflicht, meinem hochverehrten Lehrer Herrn Prof. Dr. M. Chikashige für seine ständige Unterstützung für meine Arbeit an dieser Stelle meinen herzlichsten Dank auszusprechen.

On the Synthesis of the Phosphoric Acid Esters,[1] II. Synthesis of Some Glucose Monophosphoric Acid Esters and their Behavior toward Yeast.

By

Shigeru Komatsu and Ryuzaburo Nodzu.

(Received January 30, 1924)

While the authors were engaged in experimentation upon the present problem, R. Robison's article[2] on the hexose monophosphoric acid ester appeared. According to his statement, a hexose monophosphoric acid ester was produced with hexose diphosphoric acid ester in the course of alcoholic fermentation of hexose by yeast juice or zymin in presence of a phosphate, and it was also fermented by yeast juice or zymin, the rate of fermentation being equal approximately with that of a mixture of phosphate and glucose.

C. Neuberg and his collaborators have synthesised hexose monophosphoric acid esters by the interaction of phosphorus oxychloride and some hexoses[3] or sucrose[4] in presence of calcium carbonate, and also by the partial hydrolysis[5] of hexose diphosphoric acid ester. They claimed the calcium salts of galactose and fructose phosphoric esters were fermented well by living yeast and the salt of the ester obtained by

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1 Previous article, S. Komatsu and S. Kumamoto: On Phosphoric Acid Hexahydrophenol ester, These Memoirs, **6**, 45 (1922).
2 Biochem. J., **16**, 809 (1922).
3 Ber. D. Chem. Ges., **43**, 2060 (1910); Biochem. Zs., **26**, 514 (1910).
4 Biochem. Zs., **36**, 5 (1911).
5 Ibid., **88**, 432 (1918).

the second method was fermented slowly by the same yeast, but that of glucose phosphoric ester was not fermented entirely.

These phosphoric acid esters, differing from one another in their chemical properties and especially in their behavior toward living yeast, seem to be isomeric substances ; the isomerism should be attributed to the position in which the phosphoric acid radical is attached to the sugar molecule and also the molecular structure of the sugars. The questions, however, of the isomerism and of the fate and rôle of these esters in the course of alcoholic fermentation have left unsettled.

The authors, therefore, have undertaken the present work to settle the above questions by studying the behavior of the synthesised hexose monophosphoric acid esters of known constitution and to contribute to the progress of fermentation theory.

1. Glucose-*1*-Phosphoric Acid Ester, (α or β).

This substance was obtained from tetracetyl glucose-1-phosphoric acid ester by partial hydrolysis with baryta water, which was prepared by the action of phosphorus oxychloride on pentacetyl glucose in the presence of barium hydroxide.

8 gm. pentacetyl glucose (M.P. 131°), prepared by the method of Königs and Knorr[1], were suspended in 200 c.c. of water and cooled to −5°, and then 50 gm. of barium hydroxide were added. To the mixture, 5 gm. phosphorus oxychloride dissolved in 50 c.c. dry ether, were added from a dropping funnel under vigorous stirring. The stirring was continued for 3 hours after all of the phosphorus oxychloride solution had been added, and the reaction product was made up to 800 c.c. with water, and 32 gm. of barium hydroxide were added. The mixture was shaken for 24 hours at room temperature, filtered and the residue was washed several times with conc. baryta water until no more chlorine ion was present in the washing. The insoluble residue was then extracted with 400 c.c. of water, and the

[1] Ber. D. Chem. Ges., **34**, 957 (1901).

extraction was repeated five times. The extracts combined together, carbon dioxide was passed, and the carbonate was filtered. The filtrate was concentrated to a small volume under diminished pressure, and there appeared barium carbonate which was filtered off. The filtrate was poured into a large volume of absolute alcohol, where the barium salt of the ester was precipitated. The salt thus obtained (amounting to 2 gm.), was purified by precipitation with absolute alcohol from its aqueous solution.

The purified salt, dried at 78° in vacuo on phosphorus pentoxide, was analysed : it gave C=17·70 ; H=2·97 ; P=7·64 ; Ba=34·70 ; Ash=56·53 ; ($C_6H_{11}O_6PO_3Ba$ requires C=18·21 ; H=2·81 ; P=7·84 ; Ba=34·73 ; Ash=56·74 as $Ba_2P_2O_7$). The specific rotatory power in the aqueous solution was :

$$[\alpha]_D^{23°} = +\frac{0{\cdot}68 \times 100}{4{\cdot}551 \times 1} = +14{\cdot}9°$$

It was a white powder and reduced Fehling's solution only when it was subjected to prolonged boiling with the solution or to hydrolysis with dilute acid. It yielded an osazone when the salt was heated on a water bath with phenyl hydrazine in presence of acetic acid, which melted at 203–204°. The barium salt was precipitated by alkali from its aqueous solution, but not by lead acetate. The ester, on hydrolysing with acid, yielded a substance of strong dextrotatory power.

Considering the method of formation of the ester and its properties above mentioned, it will be decided that the phosphoric acid radical of the ester is attached to the terminal aldehydic carbon atom of the glucose molecule.

2. Glucose-*3*-Phosphoric Acid Ester.

This substance was prepared from 1-2-5-6-diacetone glucose-3-phosphoric acid by partial hydrolysis, which was obtained by the action of phosphorus oxychloride on diacetone glucose[1] (M.P. 109–110°, $[\alpha]_D^{26°}$

[1] K. Freundenberg and 0. Ivers : Ber. D. Chem. Ges., **55**, 929 (1922).

$=-18{\cdot}7°$) in almost the same manner as P. A. Levene and G. M. Meyer[1].

5 gm. of the thoroughly dried diacetone glucose were reacted with 2·7 gm. phosphorus oxychloride in presence of dry pyridine, at a low temperature such as −35° by cooling with a mixture of solid carbon dioxide and ether. The reaction product was alkalined with barium hydroxide, and pyridine was removed by distillation under reduced pressure. To remove chlorine ion, it was kneaded with silver sulphate in a morter, and the excess of silver was removed by sulphuretted hydrogen. An excess of barium hydroxyde was added, carbon dioxide passed into the solution and filtered. The filtrate was concentrated under diminished pressure to a small volume, and then poured into a large volume of absolute alcohol. Leaving the solution standing over night, a translucent gelatinous precipitate was formed which was filtered and dried in a desiccator on calcium chloride. The filtrate was concentrated under reduced pressure and then allowed to evaporate to dryness in a desiccator. Both substances were almost insoluble in alcohol and acetone, and were one and the same differing only in content of diacetone glucose as an admixture, and the latter substance, therefore, was removed by extraction with ether. The yield of the pure substance free from diacetone glucose was about 6 gm. which was dried in vacuo on phosphorus pentoxide at 100° and was analysed : it gave C=29·98 ; H=4·40 ; P=6·64 ; Ba= 27·24 ; Ash=46·60 ; ($C_{12}H_{19}O_6PO_3Ba$ requires C=30·29 ; H=4·00 ; P=6·53 ; Ba=28·89 ; Ash=47·18 as $Ba_2P_2O_7$;).

The specific rotatory power in water solution :

$$[\alpha]_D^{18°}=+\frac{0{\cdot}63\times 100}{9{\cdot}134\times 1}=+6{\cdot}80°$$

which was quite different from that ($[\alpha]_D^{20°}=-2.48°$) of the barium salt of 1-2-5-6-diacetone glucose phosphoric acid mentioned by Drs. P. A. Levene and G.M. Meyer[2]. The analytical data agree with that for the

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[1] J. Biol. Chem., **43**, 236 (1921).

[2] Loc. cit. ; J. Biol. Chem., **53**, 43 (1922).

barium salt of diacetone glucose phosphoric acid. It did not reduce Fehling's solution unless it was previously hydrolysed with acid. It is strange that the specific rotatory power and the solubilities in alcohol and acetone coincide well with those of Levene and Meyer's barium salt of 1-2-monoacetone glucose-3-phosphoric acid.

To remove the acetone radical from the ester, 2 gm. of the barium salt of 1-2-5-6-diacetone glucose-3-phosphoric acid dissolved in 100 cc. of $\frac{N}{2{\cdot}5}$ sulphuric acid and kept at 40° for 24 hours. The reaction product was neutralysed with barium carbonate and made alkaline slightly by barium hydroxide and filtered, and the filtrate was concentrated to one half of the original volume under diminished pressure and filtered again. The filtrate concentrated under reduced pressure to a small volume, poured into absolute alcohol, making the concentration of alcohol to 75 per cent. Whereas the barium salt was precipitated, filtered, washed with 80 per cent alcohol, and dried on calcium chloride in a vacuum desiccator. The yield was 1·1 gm.

The sample dried at 78° in vacuo on phosphorus pentoxide, was analyzed: it gave C=18·22; H=3·27; P=7·25, 7·38; Ba=33·45, 31·17; Ash=56·19; ($C_6H_{11}O_6PO_3Ba$ requires C=18·21; H=2·81; P=7·84; Ba=34·73; Ash=56·74 as $Ba_2P_2O_7$;). The specific rotatory power in water solution, after 20 minutes:

$$[\alpha]_D = +\frac{0{\cdot}95 \times 100}{3{\cdot}241 \times 1} = +29{\cdot}2°$$

which diminished slightly after 24 hours. The aqueous solution reduces Fehling's solution easily.

The ester was designated glucose-3-phosphoric acid ester, since we admitted no transposition of the phosphoric acid group had occurred during the above treatment.

3. Glucose-*6*-Phosphoric Acid Ester.

It was prepared analogously with the preparation of glucose-6-

sulphuric acid described by H. Ohle[1] and T. Soda[2].

16 gm. of the dried powdered glucose were suspended in 80 c.c. of dry pyridine. The mixture, under cooling to −5° and vigorous stirring, was reacted with 12 gm. phosphorus oxychloride in 30 c.c. of chloroform, keeping down the reaction temperature so that it should not rise above 0°. The reaction product was allowed to remain at −5° for 3 hours after all of the phosphorus oxychloride had been added and then ice water was added. It was then brought to room temperature and stirred over night. The solution was subjected to distillation under diminished pressure to remove pyridine, and diluted with water and alkalined distinctly with baryta water, and then filtered. The excess of barium was removed by means of carbon dioxide, and the filtrate from barium carbonate was concentrated under reduced pressure to a syrup. To remove hydrochloric acid from the syrup, it was diluted with water and treated with silver sulphate, and then with sulphuretted hydrogen. When the latter had been removed by a current of air, the solution was filtered and a small excess of barium hydroxide was added and carbon dioxide was passed. The solution free from barium carbonate, was concentrated under diminished pressure and poured into absolute alcohol, the concentration of alcohol was kept in the neighbourhood of 75 per cent. The barium salt precipitated was separated from the solution by centrifuging, washed with 75 per cent alcohol, and again centrifuged. The barium salt, thus obtained, weighed 3·5 gm.

For the purification, it was dissolved in a small volume of water, alkalined with baryta water, filtered and precipitated with absolute alcohol and then washed with 80 per cent alcohol. The precipitate was dissolved again in water and filtered and then neutralized with carbon dioxide. The precipitate dried to constant weight under reduced pressure on phosphorus pentoxide at 78°, and analyzed: it gave C= 18·61; H=3·28; P=8·42; Ba=33·81; ($C_6H_{11}O_6PO_3Ba$ requires C=

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[1] Biochem. Zs., **131**, 601 (1922).
[2] Ibid., **135**, 621 (1923).

18·21 ; H=2·81 ; P=7·84 ; Ba=34·73 as $Ba_2P_2O_7$;). The specific rotatory power in water solution :

$[\alpha]_D = +\frac{0{\cdot}66 \times 100}{3{\cdot}460 \times 1} = +19{\cdot}1°$; whence $[\alpha]_D = +29{\cdot}0°$ for the free ester. The rotatory power diminished a little after 24 hours. The salt is a white power and reduces Fehling's solution readily.

The allocation of phosphoric acid radical in the glucose molecule was assigned to be the 6th carbon atom from analogy with the sulphuric acid ester[1] and also from the chemical properties of the ester.

4. Neuberg's Glucose Phosphoric Acid Ester[2].

The calcium salt of this ester was prepared by the action of phosphorus oxychloride on glucose in the presence of calcium carbonate. The salt dried to constant weight in vacuo on sulphuric acid, was analyzed : it gave C=21·82 ; H=4·23 ; P=9·69 ; ($C_6H_{11}O_9P\,Ca+2H_2O$ requires C=21·55 ; H=4·49 ; P=9·28 ;). The specific rotatory power in aqueous solution :

$[\alpha]_D^{15°} = +\frac{0{\cdot}68 \times 100}{2{\cdot}316 \times 1} = +29{\cdot}3°$(after 20 minutes)

$[\alpha]_D^{15°} = +\frac{0{\cdot}58 \times 100}{2{\cdot}316 \times 1} = +25{\cdot}0°$(constant) and that calculated as free esters $[\alpha]_D = 30{\cdot}5°$

Accordingly the Neuberg's ester seems to be the same substance as the 6-phosphoric acid ester.

5. Behavior of the Esters toward Yeast and Zymin.

In the experiment, the aqueous solution of the sodium salts of the esters was used which prepared by neutralizing the free esters with sodium hydroxide using phenolphthalein as indicator. The free esters were formed by the interaction of barium or calcium salts of the esters and calculated quantities of sulphuric acid and centrifuging off

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1 Loc. cit.
2 Loc. cit.

the sulphate. The velocity of fermentation was determined by measuring the volume of carbon dioxide generated, using Einhorn's fermentation saccharometer. The yeast employed, was a fresh pressed bottom yeast from the Suita brewery (Dai Nippon Bakushu Kabushiki-kaisha, Suita, near Osaka).

Exp. I.

(a) 10 c.c. 2 per cent (calc. as free ester) solution of the 1-ester+1 gm. pressed yeast.

(b), (c) and (d) 3–, 6– and Neuberg's esters respectively with pressed yeast.

(e) 10 c.c. 2 per cent glucose solution+1 gm. pressed yeast. These were incubated at 26° and the quantity of CO_2 measured in c.c.

Time (in hr.)	(a)	(b)	(c)	(d)	(e)
2	0·3	0	0·3	0	6·0
5	"	"	"	0·1	—
6	"	"	"	"	—

None of the esters, as seen in the experimental results, was fermented by the yeast.

Exp. II.

The action of Schroder's zymin on the esters was studied, and the zymin was prepared according to the directions of A. Harden.[1]

(a) 10 c.c. 2 per cent (calc. as free ester) solution of the 1–ester+1 gm. zymin+0·1 c.c. toluene.

In (b), (c) and (d) the 1–ester in (a) was replaced by 3–, 6– and Neuberg's esters respectively.

(e) 10 c.c. of the 1·38 per cent glucose solution (equivalent to the esters) +1 gm. zymin+0·1 c.c. toluene+0·05 gm. of $Na_2HPO_412H_2O$: These were incubated at 25° and the quantity of CO_2 was measured in c.c.

Time (in hr.)	(a)	(b)	(c)	(d)	(e)
1·0	0·4	0·3	0·1	0	2·0
1·5	0·8	1·4	0·6	0·1	3·0
2·0	1·5	2·4	1·2	0·2	3·5
2·5	2·4	3·3	1·8	0·25	4·2
3·0	3·5	4·1	2·2	0·4	4·8

All of the esters were fermented by zymin, and especially 1-and 3-esters

[1] A. Harden: Alcoholic Fermentation 1923, p28.

worked more rapidly.

Exp. III.

(a) 15 c.c. 5 per cent glucose solution+3 c.c. 2 per cent solution of the 1-ester (calc. as free ester)+1 gm. zymin+0·1 c.c. toluene.

In (b), (c) and (d) the 1-ester in (a) was replaced by 3–, 6– and Neuberg's esters respectively.

(e) 15 c.c. 5 per cent glucose solution+3 c.c. Na_2HPO_4 solution (0·274 gm. Na_2HPO_4 12 H_2O in 10 c.c., equivalent to the esters)+1 gm. zymin+0·1 c.c. toluene.

(f) 15 c.c. 5 per cent glucose solution+3 c.c. H_2O+1 gm. zymin+0·1 c.c. toluene.

These were incubated at 24° and the quantity of CO_2 was measured in c.c.

Time (in hr.)	(a)	(b)	(c)	(d)	(e)	(f)
1·0	0·2	0·2	0·2	0·2	0·2	0·3
1·5	0·5	0·5	0·3	0·4	0·6	0·4
2·0	0·9	0·7	0·5	0·6	1·3	0·5
2·5	1·25	1·1	0·75	0·8	1·95	0·7
3·0	1·65	1·35	1·1	1·05	2·7	0·8
3·5	2·1	1·8	1·5	1·4	3·3	1·0

Among the esters, 1–and 3–esters exert some positive effects on the zymin action.

Exp. IV

(a) 15 c.c. 5 per cent glucose solution+4 c.c. of the 2 per cent solution of the 1-ester (calc. as free ester)+ a residue obtained from 2 gm. zymin by washing with water 3 times+0·1 c.c. toluene.

(b) and (c) the 1-ester in (a) was replaced by the 3-and 6-esters respectively.

(d) 15 c.c. 5 per cent glucose solution+4 c.c. H_2O+ the washed zymin +0·1 c.c. toluene.

These were incubated at 24° and gas was measured in c.c.

Time	(a)	(b)	(c)	(d)
11·5 hrs.	0	0	0	0
4 days	0	1·5	0	0

Exp. V.

In (a), (b), (c) and (d) the mixtures of the corresponding cases in Exp.

IV had added 1 c.c. 10 per cent $Na_2HPO_4 12H_2O$ solution respectively.

Time	(a)	(b)	(c)	(d)
12 hrs.	0	0	0	0
4 days	2·4	7·0	3·0	2·0

(In (d), after one day, some water extract of zymin was added.)
Iodoform reaction in the fermented liquids was positive.
The mixture of glucose and the 3–ester was fermented by the washed zymin, while that of glucose and other esters were fermented very slowly only when they were accompanied by sodium phosphate.

From these results the following conclusions are drawn :

1. None of the esters was fermented by living yeast while the 1– and 3– phosaphoric acid esters, on the one hand, were fermented rapidly by zymin, the rate being approximately equal to that attained with a mixture of phosphate and glucose, and other hand, they accelerate the fermentative action of zymin on glucose. It was, therefore, concluded that the 1– and 3–esters will maintain some important relation to the alcoholic fermentation of sugars in presence of phosphate.
2. Moreover, the fact that the 3–ester 4 days after the experiment had started, began to accelerate the action of zymin, freed from the co-enzyme, on glucose with or without phosphate, which suggested that some resemblance in behavior existed between the ester and co-enzyme.
3. Now, it is highly probable that the hexose monophosphoric acid ester, taking the investigation of Robison into consideration, will play an important rôle in the alcoholic fermentation of sugars as the di-phosphoric acid ester does, which was fully revealed by the extensive investigation of A. Harden and W. J. Young[1]. Admitting that Robison's statement was correct, the idea was naturally deduced that some of our esters will actually be formed in the course of the alcoholic fermentation of sugars in presence of phosphate by yeast juice.
4. Among them all, the 3–phosphoric acid ester from its behavior

[1] Proc Chem. Soc., **21**, 184 (1905); Proc. Roy. Soc. B, **80**, 299 (1908); Ibid., **81**, 336 (1909); Ibid., **82**, 321 (1910); Biochem. Zs., 173, 178 (1911); Proc. Roy. Soc. B, **81**, 525 (1909).

towards zymin or washed zymin, was regarded as the very ester which the authors had expected would be formed in the fermentative liquor. Final decision, however, was postponed until further work should be done, since none of our esters coincide, in specific rotatory power, with Robison's ester.

Nov. 1923. Laboratory of Organic- and Bio-Chemistry.

Studies on Camphor Series, IV.

By

Shigeru Komatsu and Chikau Fujio.

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I. THE ELIMINATION OF HYDROGEN CHLORIDE FROM PINENE HYDROCHLORIDE AND BORNYL CHLORIDE.

In finding a suitable catalyst for the preparation of camphene from the corresponding terpene monochloride, the catalytic action of the chlorides of iron, copper, antimony, aluminium, barium, magnesium and phosphorus on pinene hydrochloride and bornyl chloride was investigated[1].

Pinene was obtained from the terpentine oil (pharm. Jap.) by repeated fractional distillations on metallic sodium, the fraction B. p. 156–161° $[\alpha]_D^{25°} = -2{\cdot}19°$ was transformed into pinene hydrochloride by passing dry hydrochloric acid gas, and cooling with ice[2].

It melts at 125°, showed $[\alpha]_D^{25°} = -4{\cdot}72°$ in alcohol solution.

Bornyl chloride was prepared from dextro-borneol M. p. 127°, $[\alpha]_D^{25} = +17{\cdot}21°$ in alcohol solution (d-borneol 71·73% isoborneol

1 Refer W. F. Faragher and F. H. Garner: J. A. C. S., **43**, 1715 (1921); P. Sabatier and Mailhe: C. R., **138**, 407 (1904); **141**, 238 (1905); P. Sabatier and Sanderens: Ibid., **146**, 1211 (1908); J. Nef: Lieb. Ann., **318**, 1 (1901); O. Wallach: Lieb. Ann., **239**, 6 (1887); O. Aschan: Ber. D. Chem. Ges., **40**, 2750 (1907); Lieb. Ann., **387**, 27 (1912); **410**, 222 (1915); J. Kondakow: J. prak. Chem., **54**, 452 (1896).

2 B. T. Brooks: The Non-benzenoid Hydrocarbons, 439 (1922).

28·27%), and phosphorus pentachloride, which melts at 148°, and showed $[\alpha]_D^{25°} = +12·93°$ in alcohol solution.

In the experiment, 1 grm. of the sample was mixed with 2 grm. of the catalyst in a sealed tube and heated at a temperature of 100° and 200° by means of a water bath or an air bath. After heating for a certain time, the reaction product was subjected to steam distillation, and the amount of unsaturated hydrocarbon which resulted as a dechlorinated product, and was distilled with steam, was calculated from the iodine number estimated as usual. The results are shown in the following table:

Pinene hydrochloride
100°
yield (in %)

Times (in Minutes)	$FeCl_3$	Al_2O_3	$AlCl_3$	$BaCl_2$	$MgCl_2$	$SbCl_3$	PCl_3
10	60	20	23	—	32	60	—
20	70	17	31	—	32	62	—
30	55	17	33	14	—	64	35
60	43	17	44	19	35	56	90
90	40	18	29	16	35	48	80
120	65	17	44	19	—	60	79
150	25	15	33	—	—	—	—
180	20	—	27	—	—	—	—
210	25	—	26	—	—	—	—

Pinene hydrochloride
200°
yield (in %)

Times (in Minutes)	$FeCl_3$	Al_2O_3	$AlCl_3$	$BaCl_2$	$MgCl_2$	$SbCl_3$	PCl_3
15	25	56	39	0	31	15	—
30	28	44	56	0	—	18	—
60	18	29	50	0	25	11	—
90	18	15	32	0	21	11	—

Bornyl chloride and $FeCl_3$
yield (in %)

Times (in Minutes)	100°	200°
10	2	0
20	3	0
30	4	1
60	3	0·5
90	5	0
120	3	0
150	3	0
180	6	0
210	6	0
240	2	0

As seen in the foregoing table, ferric chloride is the most active catalyst up to 100°, while a higher temperature, such as 200°, alumina and aluminium chloride serve more effectively than other catalysts.

As we had previously discovered in the case of the reaction between aniline and monochloroacetic acid[1], the reaction in a closed vessel is more complicated than that in an open vessel; unsaturated hydrocarbon formed by the dechlorination, remaining in the reaction tube with hydrochloric acid, unchanged chloro compound and the catalyst, is apt to recombine on one hand with hydrochloric acid, forming camphene hydrochloride which will be soon transformed into stable isobornyl chloride[2], and on the other hand, to react with the chloro compound remaining unchanged or formed by isomeric change by virtue of the catalyst as in the case of Friedel–Crafts' reaction, generating a condensed hydrocarbon of higher molecules[3], as will be shown in the following schemes:

1 S. Komatsu and R. Nodzu: These Memairo, **6**, 73 (1922).
2 H. Meermein and K. van Emster: Ber. D. Chem. Ges., **53**, 1815 (1920).
3 K. Bartelt: Terpene u. Campherarten, 110 (1908); J. Kachler: Ber. D. Chem. Ges., **2**, 510 (1869); J. Kondakow: J. prak. Chem., **54**, 452 (1896); K. G. Falk: Chem. Reaction, 95 (1920).

$$C_{10}H_{17}Cl \xrightarrow{-HCl} C_{10}H_{16} \xrightarrow{+HCl} C_{10}H_{16}HCl$$

$$C_{10}H_{16}+C_{10}H_{16}HCl \longrightarrow C_{10}H_{16} \cdot C_{10}H_{16}+HCl.$$

Thus, the catalyst serves to separate the hydrogen chloride from the pinene hycrochloride or bornyl chloride forming in the way camphene which is added to the unchanged pinene hydrochloride or bornyl chloride by the iufluence of the same catalyst to form a compound such as dibornylene.

Moreover, the catalyst will play a role as polymerising agent of the unsaturated hydrocarbon to condense to higher molecule content.

Accordingly, it was anticipated that when the reaction proceeded, the yield of volatile unsaturated hydrocarbon would be gradually diminished with time. Such a hypothesis harmonizes with the experimental results as seen in the table. For confirmation of the hypothesis, we tried to isolate the compound which was considered to be formed from camphene and camphene hydrochloride or bornyl chloride and actually we succeeded in getting a hydrocarbon of the molecular formula $C_{20}H_{32}$ from the reaction product.

25 grm. pinene hydrochloride and 25 grm. ferric chloride were heated in a sealed tube at 100° for one hour, the reaction product was subjected to steam distillation and the non-volatile substance remaining in the flask was a dark brown mass which was extracted with ether. On distilling off the solvent, there remained a brown viscous oil which distilled out from 320° to 340°; the yield was 1·2 grm. After repeated fractional distillations on metallic sodium, the fraction boils at 208–210° 10 mm., was analysed :

C=88·93 ; 89·13 ; H=11·23 ; 11·44. $n_D^{25°}=1·5304$; $d_4^{25°}=0·9649$.

The analytical figures agree with C=88·88 ; H=11·12 for $C_{20}H_{32}$.

When bornyl chloridew as used instead of the pinene hydrochloride, the product had the same appearance as that obtained from pinene hydrochloride, boiled at 189°, 12 mm., and gave on analysis the following results :

C=89·40 ; H=10·34. $d_4^{25°}$=0·9633 ; $n_D^{25°}$=1·5285.

Moreover, the molecular weight determination of the first sample in benzene solution showed M. W.=283 which agrees the required value for $C_{20}H_{32}$.

On reduction with hydrogen, 0.1499 grm. of the substance absorb 12.3 c.c. hydrogen in presence of colloidal palladium, which indicate it contains one ethylene bond in the molecule as we expected.

II. SOLID AND LIQUID MODIFICATIONS OF CAMPHENE.

In the previous article, one of the authors (S. Komatsu) and R. Nakai[1] have reported that there exist two modifications of camphene, one, liquid at ordinary temperature B. p. 158–162°, $d_4^{25°}$=0·8613 ; $d_D^{25°}$= 1·4689 and the other, a solid M. p. of 50°.

According to Brühl[2], camphene is prepared from pinene hydrochloride, melting at 51–52°, B. p. 158·5–159·5°, $n_D^{25°}$=1·4551 and the same substance derived from bornyl chloride, melting at 53·5–54°, d_4^{58}=0·83808; $n_D^{58°}$=1·54314.

The authors, therefore, intended to get two modifications of camphene from one and the same substance, and compare their physical properties, and whereby to ascertain the nature of the modifications.

50 grm. of pinene hydrochloride were heated with 10 grm. anhydrous ferric chloride in a flask with reflux condenser at 210–215° for 1½ hours, and the reaction product was subjected to distillation. The product collected between 150–164°, was washed with water and

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1 These Memoirs : **6**, 70 (1922).

2 Ber. D. Chem. Ges., **25**, 147, 160 (1892).

distilled on metallic sodium after drying with sodium sulphate as usual. The yield of fraction B. p. 150–165°, was 25 grm., 160 grm. of the hydrocarbon, thus obtained, were fractionated under ordinary pressure into 10 portions, and each portion was analysed and its properties determined.

Fractions	Yield	$n_D^{25°}$	$d_4^{25°}$	C	H
145—150°	8·5	1·4550	0·84834	87·53	12·37
150—152	14·0	1·4574	0·85224	86·69	12·07
152—154	36·5	1·4597	0·85560	87·41	11·98
154—156	15·5	1·4621	0·85838	87·62	12·08
156—157	18·0	1·4629	0·85868	87·33	11·83
157—158	18·0	1·4639	0·85974	87·64	11·94
158—159	5·0	1·4642	0·85886	87·64	12·13
159—162	12.0	1·4651	0·85838	87·06	12·04
162 - 164	5·0	1·4667	0·85828	87·17	12·02
above 164	4·5	1·4696	0·85806	—	—

Cal. for $C_{10}H_{16}$ 88·12 11·88
Cal. for $C_{10}H_{18}$ 86·95 13·05

When pinene hydrochloride was dechlorinated with the same catalyst at a lower temperature 125-135°, it yielded as a result a solid hydrocarbon with the same composition as liquid camphene.

The reaction product obtained by the interaction of 25 grm. pinene hydrochloride and 10 grm. ferric chloride at 125–135° for 1½ hours, which was distilled and collected, the fraction boiling to 195°. The boiling point of the product by heating with metallic sodium was found to be depressed from 170–195° to 150–165°. From 140 grm. of the reaction product, 25 grm. of the liquid substance and 115 grm. of the solid were separated.

The solid substance was fractionated into 7 portions and each fraction distillation 13 times, was analysed.

Fractions	Yield	M.p.	C	H
to 152°	3·5			
152—154	10·5	42—37	87·37	12·15
154—155	12·0	49—50	87·37	11·97
155—156	14·5	56—57	87·28	11·98
156—157	12·5	60—61	87·87	12·01
157—158	12·0	65—67	87·42	11·78
158—159	2·0	—	—	—
above 159	3·5	—	—	—

Calc. for $C_{10}H_{16}$ 88·12 11·88
Calc. for $C_{10}H_{18}$ 86·95 13·05

Fractions	$n_D^{58°}$ (Liquid)	$n_D^{58°}$ (Solid)
152—154°	1·4432	1·4415
154—155	1·4443	1·4657
155—156		1·4662
156—157	1·4478	1·4665
157—158	1·4478	1·4678
158—159	1·4485	1·4687

Fractions	$d_4^{70°}$ (Liquid)	$d_4^{70°}$ (Solid)	$n_D^{70°}$ (Liquid)	$n_D^{70°}$ (Solid)	M. p.
152—154°	0·82260	0·82318	1·4367	1·4351	42—47
154—155	0·82556	0·82498	1·4376	1·4361	49—50
155—156		0·82615		1·4370	56—57
156—157	0·82585	0·82674	1·4385	1·4380	60—61
157—158	0·82615	0·82733	1·4400	1·4394	65—67

The physical constants of some fractions of the liquid modification were measured at 25°, 58°and 70°, and the results were compared with those of the corresponding fractions of the solid.

Further researches are required to attain the desired conclusion about the true nature of these modifications, and these researches will be undertaken in our laboratory.

Nov. 1923. Laboratory of Organic-and Bio-Chemistry.

On the Biochemical Study of the Ripening of the Kaki-Fruit,[1] VII.

By

Shigeru Komatsu and Motaro Ishimasa.

(Received Jaunary 30, 1924)

I. ARE THERE ANY DIFFERENCES IN CHEMICAL COMPOSITION BETWEEN THE ASTRINGENT AND SWEET VARIETIES?

On comparing the ultimate analysis of both varieties mentioned in Sawamura's article, one of the authors (S. K.) and H. Ueda[2] are inclined to believe that there was no marked difference in the composition.

When, however, comparing the percentage composition of sugars, pectin, shibu and acids in the pulp of both fruits, the difference to distinguish one from the other came to our notice.

For comparison, the authors have made the analysis of three strains of the sweet variety and of four strains of the astringent one, all grown on the same ground at Tanaka, Kyoto[3]. Three fruits were picked from each tree at a different stage of growth, and were analysed as usual. In Table I, all of the figures are the percentage distribution

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1 The expenses of this investigation were shared by the Government Department of Education.

2 J. Biochem., **1**, 181 (1922).

3 Refer second article, S. Komatsu and H. Ueda: J. Biochem., **2**, 291 (1922), Fifth article, S. Komatsu and M. Ishimasa: Ibid., 3, (1924); and Sixth article, S. Komatsu and M. Ishimasa: these Memoirs, 7, 165 (1924).

of the constituents of the fruit in the pulp, and those in Table II. are the mean value of the percentage composition of the constituents in each month.

Studying precisely the figures on the tables, the following conclusion were summarised.

(1) The astringent fruit, when it is young, contains less sugar and much pectin, shibu and acid compared with the sweet one picked in the same season.

(2) The sugar-content in the astringent fruit increases with greater velocity than in the sweet one, while the pectin-content in the former decreases much more than in the latter.

(3) The soluble shibu and acids-contents are rich in the astringent fruit, and moreover, the velocity of their disappearance in the astringent fruit is slow compared with that in the sweet one.

(4) The percentage composition of these substances in the two varieties, showed a marked difference in their unripe state, they, however, approarch very nearly to each other when the fruits have attained their maturity, actually no distinction being found between the two fruits in state.

II. ON THE CURING PROCESS.

Keeping a fruit dried and cured by the process was, in this country, usually regarded as the best way for its preservation.

On subjecting the fruit to a desiccating process, it was an important thing to bring the fruit to a suitable condition in the minimum time, preventing the consumption of sugars by respiration and by fermentation as far as possible. Since, as has been already shown, the full-grown astringent fruit was left to stand at the room-temperature for a while, not only was one part of the sugars in the fruit consumed by its respiration decomposing into carbon dioxide and water, but also by the fermentation transforming it into alcohol and

other substances[1].

To find the most suitable conditions for carrying out this purpose of preparing the fruit for drying, the following preliminary experiments were carried out with the fruit named " Daishiro " grown on Mr. Uno's farm, Tanaka.

(1) One ripe fruit weighing 74·5 grm. was divided into two parts, one part was soon analysed and the remainder was left without any treatment for 6 days in the laboratory.

The loss of sugar and of water in 6 days was 7·5% and 20·5% respectively, while the acid–content was increased (0·002 grm.) due to the fermentation of sugars.

(2) The peeled fruit was kept for 8 days in the laboratory, and then analysed, the results were compared with those of the whole fruit kept for 8 days for control under the same condition.

In the former, 4% of sugar and 17% of water, while in the latter 2% of sugar were lost, while the water–content in the latter remained constant. In both fruits sucrose was inverted completely into the reducing sugars, and it was confirmed that the acrid taste had disappeared.

(3) In the third experiment, one fruit was divided into two parts, one of which was peeled and analysed after keeping 8 days in the laboratory, and the results were compared with those of another half which was analysed, for control, soon after peeling. By this treatment, the loss of sugar and water was 17·5% and 48% respectively.

Consequently, it was concluded from the above statement that in the desiccating process the peeled fruit loses less sugar by respiration and by fermentation but much water by evaporation compared with the results of other treatments.

Nov. 1923, Laboratory of Organic– and Bio–Chemistry.

1 Pasteur : C. R., **75**, 1056 (1872) ; Lechartier e. Bellamy : Ibid., **75**, 1204 (1872) ; **79**, 949 (1874) ; F. Czapeck : Biochem. Pflanzen., **1**, 422 (1913).

Table I.

ASTRINGENT VARIETY.

Daishiro.

Percentage in Pulp.

Date.	Reducing Sugar.	Cane Sugar.	Total Sugar	Pectin.	Shibuol.	Acid.	Water.
July 10.	3·24	0·40	3·63	—	—	—	—
„ 12.	3·29	0·33	3·61	2·23	1·54	0·24	80·9
Aug. 9.	4·01	2·13	6·13	1·75	1·61	0·18	81·1
Sep. 10.	4·51	3·44	7·94	1·82	1·56	0·15	81·7
Oct. 3.	7·36	3·45	10·80	—	—	—	—
„ 15.	10·68	0·60	11·28	1·16	0·65	0·09	81·3

Daishiro.

Percentage in Pulp.

Date.	Reducing Sugar.	Cane Sugar.	Total Sugar.	Pectin.	Shibuol.	Acid.	Water.
Sep. 27.	10·01	1·40	11·41	1·87	0·69	0·11	79·7
„ „	8·92	2·29	11·21	1·95	0·40	0·08	77·6
Oct. 22.	11·88	0·83	12·71	1·43	0·41	0·05	80·0

SWEET VARIETY.

Gosho-Gaki.

Percentage in Pulp.

Date.	Reducing Sugar.	Cane Sugar.	Total Sugar.	Pectin.	Shibuol.	Acid.	Water.
July 13.	3·39	1·29	4·68	1·72	0·86	0·17	80·0
Aug. 10.	4·08	2·86	6·95	1·73	0·31	0·09	81·1
Sep. 11.	4·76	4·26	9·03	1·44	0·16	0·06	82·5
Oct. 3.	5·76	4·46	10·22	—	—	—	—
„ 16.	8·29	3·62	11·91	1·49	—	0·08	80·3

Ansai.

Percentage in Pulp.

Date.	Reducing Sugar.	Cane Sugar.	Total Sugar.	Pectin.	Shibuol.	Acid.	Water.
Sep. 25.	6·88	3·18	10·65	1·99	0·60	0·05	80·6
Oct. 19.	9·15	2·19	11·34	1·32	—	0·06	80·0

Kubo-Gaki.

Percentage in Pulp.

Date.	Reducing Sugar.	Cane Sugar.	Total Sugar.	Pectin.	Shibuol.	Acid.	Water.
Oct. 1.	8·13	1·53	9·65	1·65	0·34	0·11	80·4
,, 23.	8·75	2·36	11·11	1·47	0·21	0·07	81·2

Table II.

Percentage in Pulp.

Month.	Total Sugar.		Pectin.		Shibuol.		Acids.	
	S.	A.	S.	A.	S.	A.	S.	A.
7	5	4	1·7	2·1	0·9	1·5	0·17	0·3
8	7	5·5	1·7	1·7	0·3	1·8	0·09	0·2
9	9·5	8·0	1·6	1·7	0·4	1·5	0·06	0·16
10	11	11	1·4	1·5	0·2	1·1	0·07	0·10

S. . . . . Sweet variety

A. . . . . Astringent variety.

Studies on Catalytic Action, VIII.
Catalytic Reduction of β-Naphthylamine.

By

Tohoru Hara.

(Received January 30, 1924)

In previous article[1], it has been shown that naphthols when reduced catalytically yielded ac-hydro-compounds in a greater quantity compared with the case of naphthyl ethers while α-naphthylamine resulted by the same treatment in yielding much more ar-hydro-compounds.

Thus, the yield of ac- and ar-hydro-compounds seems to depend chiefly upon the electronic nature of the atomic group substituting for the hydrogen atom of the naphthalene, and upon the spatial disposition of the substituted group.

β-Naphthylamine was, therefore, reduced in presence of reduced nickel at 200°, to study whether the steric hindrance in the catalytic hydrogenation of naphthylamines would be observed as we have encountered in the cases of naphthols and their methyl ether, and consequently to verify the above statements.

The amine used in this experiment, was prepared following the direction of E. Fierz[2], from 360 grm. β-naphthol M. p. 121–122°, ammonium sulphite and ammonia, yielding 105 grm. pure amine M. p.

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1 S. Komatsu and R. Nodzu : These Memoirs, **6**, 177 (1923) ; S. Komatsu and I. Nishimatsu : Non-published results ; S. Komatsu and S. Kumamoto : These Memoirs, **7**, 135 (1924).

2 Farbenchemie, 126 (1920).

110–111°, B. p. 296–297°.

54 grm. of the amine were passed with hydrogen on the finely divided nickel prepared from 25 grm. nickel oxide by reduction, in an interval of 200 hours, and the following reaction products were obtained :

(A) 36 grm. of a dark brown liquid with some crystals.

(B) 2·36 grm. of ammonia, absorbed in the receiver containtng hydrochloric acid, which corresponds to 36·5% of naphthylamine.

(C) 14·5 grm. of a dark brown thick oil which remained with nickel in the reaction tube, and which was extracted with ether.

The reaction product (A) was fractionated and,

(D) 30 grm. of the substance distilled out to 360° and

(E) 5·5 grm. of the residue were obtained.

(D) Portion was treated with dilute hydrochloric acid to separate the neutral compound from the basic one, and the former was extracted with ether. On evaporating off the ether, there remained

(F) 10·5 grm. of an oily substance with some crystals boiling at 204–224°.

(F) Fraction was divided into three parts by fractional distillation and each part was examined.

Tetrahydronaphthalene.

The fraction, B. p. 205–207°, amounted to 7·5 grm., was purified by distillation, and was confirmed to consist of tetrahydronaphthalene by analysis and determination of physical constants :

0·0951 grm. substance gave 0·3167 grm. CO_2 and 0·0815 grm. H_2O.

	Calc. for $C_{10}H_{12}$.	Found.
C	90·84	90·82
H	9·16	9·52

$d_{4^\circ}^{25^\circ} = 0{\cdot}9673$; $n_D^{25^\circ} = 1{\cdot}5414$.

Dihydronaphthalene.

The second fraction B. p. above 207°, decolorises the potassium permanganate solution, but, further confirmation for dihydronaphthalene was lacking owing to its small quantity.

Naphthalene.

The third fraction, amounting to 0·8 grm., consists of a solid compound. The substance purified by recrystallization from alcohol solution, amounted to 0·45 grm., melting at 79–80°, and by treating with picric acid gave naphthalene picrate melting at 149–150°. For confirmation, it was analyzed with the following results:

0·1067 grm. substance gave 0·3635 grm. CO_2 and 0·0621 grm. H_2O.

	Calc. for $C_{10}H_8$	Found.
C	93·70	92·87
H	6·30	6·46

The basic substances (18 grm.) isolated from the product (D) by means of dilute hydrochloric acid, confirmed to contain no ac-hydronaphthylamine, was subjected to distillation and all was distilled out 276–284°.

β-ar-Tetrahydronaphthylamine

It was distilled twice under ordinary pressure, and once under 17–18 mm., and was confirmed to consist entirely of β-ar-tetrahydronaphthylamine. The yield of purified substance was 8·4 grm. It boils 147–151°, 17–18 mm., M.p. 38°.

0·1283 grm. substance gave 0·3828 grm. CO_2 and 0·1081 grm. H_2O.
0·1160 „ „ „ 0·3462 „ „ „ 0·0919 „ „
0·1802 „ „ „ 15 c.c. N_2, 761·2 mm. 12°.

	Calc. for $C_{10}H_{13}N$.	Found.	
C	81·57	81·37	81·39
H	8·90	9·36	8·75
N	9·52	9·65	—

It gives diazo-compound. For confirmation of the constitution of the amine, 2·0 grm. of the sample were converted to ar-tetrahydronaphthol according to the direction of Bamberger and Kitschelt[1] and 0·45 grm. pure ar-tetrahydronaphthol were obtained which melted at 59–59·5° and gave on analysis the following results:

[1] Ber. D. Chem. Ges., **23**, 884 (1890).

0·1049 grm. substance gave 0.3102 grm. CO_2 and 0·0774 grm. H_2O.

	Calc. for $C_{10}H_{12}O$.	Found.
C	81·03	80·65
H	8·17	8·19

The fraction (C) was divided into three parts by fractional distillation :

(1) 0·8 grm. hydrocarbons boiling at 210–220°,

(2) 0·8 grm. ar-hydro-amines boiling at 270-280° and

(3) 11·5 grm. of the residue.

β-β′-Di-ar-tetrahydronaphthylamine, $(C_{10}H_{11})_2NH$.

The last substance being the same as (E) and both consisting mainly of a basic substance, they were combined together and were purified by transforming into the hydrochloride. The free base recrystallized from absolute alcohol solution, was white crystals and melting at 59–60°, showed the secondary amine reaction, and gave on analysis the following results :

0·1045 grm. substance gave 0·3307 grm. CO_2 and 0·0772 grm. H_2O.
0·1158 grm. ,, ,, 0·3702 grm. ,, ,, 0·0842 grm. ,,
0·2101 grm. ,, ,, 10·6 c.c. N_2. 760·4 mm. 10°.

	Calc. for $(C_{10}H_{11})_2NH$.	Found.	
C	86·58	86·31	86·40
H	8·36	8·21	8·08
N	5·05	5·86	—
M. W.	277	282	

Molecular weight was determined by depression of the freezing point of benzene solution.

β-Naphthylamine by catalytic reduction at 200° yielded 18.8 grm. ar-tetrahydronaphthylamine, 17 grm. di-ar-tetrahydronaphthylamine and 11·3 grm. hydrocarbons, and the latter substances were considered to be derived from ac-hydronaphthylamine and corresponded to 12·4 grm. of the amine.

	Yield in mol %	
	ar-comp.	ac-comp.
α-compound	90	10
β-compound	74	26

The hypothesis when the results were compared with those of the α-isomer, was verified experimentally as the author had anticipated.

Nov. 1923. Laboratory of Organic- and Bio-chemistry.

Some Fundamental Principles of the Author's Theory of the Dispersoid[1] (Colloid) State.[2]

By

P. P. von Weimarn.

(Received March 31, 1924)

A. General Principles.

1. All the properties (both chemical and physical) which earlier were considered as specific of the colloid substances, appear spontaneously with *every* solid substance as its subdivision progressively increases, irrespective of the means by which this subdivision is brought about (e. g. whether they be chemical, physico-chemical, physical, mechanical, and the like).
2. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on dissolving, through a *colloid stage of solution.*

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1 The terms: "*Dispersoid*", "*Dispersoidal*" were in due time suggested by myself to be used instead of the terms: "Colloid", "Colloidal" which latter have entirely lost, according to my opinion, their original value. The general science dealing with the dispersoid state I proposed to call "*Dispersoidology*", to be conveniently subdivided further into Dispersoid Physics and Dispersoid Chemistry, or still shorter: *Dispersoidics* and *Dispersoidy* correspondingly / The corresponding German terms are:

Dispersoidologie ⟨ Dispersoidphysik = Dispersoid(phys)ik = *Dispersoidik.*
Dispersoidchemie = Dispersoid(chem)ie = *Dispersoidie.*

It should be noted here that the term "Dispersoidik" was suggested for the first time by *Wo. Ostwald* (see: Koll.-Zeitschr. **33**, 300. 1923), but somewhat in a different sense/. I maintain that the short terms: "Dispersoidics" and "Dispersoidy" are most convenient for designating correspondingly the physics and the chemistry of the dispersoids.

2 Compare the present paper with my paper of analogical contents in "News of the Ural Mining Institute", Vol. 1 (1918/19); Section III; pp. 65–69.

And in fact, if, with a size of the crystalline grains falling below the limits of microscopic resolvability, the colloid properties (Principle I) begin to assert themselves somewhat sharply, it is obvious that, were we to stir up a pinch of some powdered substance in a liquid in which it is able to dissolve, the grains of this powder must necessarily pass through a *colloid stage of solution*, antecedent to their complete dissolution, i. e. before they break up into molecules (in special cases – into atoms).

For the cases of solid substances *rapidly* dissolving in the liquids selected, the time intervals during which this *colloid stage* of solution would persist, will naturally be very small; but nevertheless, even for these cases, the existence of a *colloid stage of solution* is beyond any doubt.

3. Any solid substance, regardless of what its chemical nature or any of its other properties may be, must always pass, on crystallizing, through a *colloid stage of crystallization*.

For the cases of a *rapid* increase in size, i. e. of rapid growth of the vanishingly small crystals initially formed, the time intervals during which the *colloid stage* of crystallization would persist, will naturally be very small, but nevertheless, even for these cases, the existence of a *Colloid stage of crystallization* is beyond any doubt.

4. For any substance such physico-chemical conditions of crystallization and solution may, according to one's wish, be realized, at which the colloid stages of crystallization and solution would last for periods of time, of which the corresponding durations may be varied, according to the above mentioned conditions, within extremely wide limits, viz.: from such practically vanishingly small values as amount to e. g. fractions of a second and seconds, up to such large values as are measured by years, decades and even centuries.
5. For *any* given solid substance, suitable solvents and such temperature conditions may be found, at which, in the solutions of this solid substance in the above solvents, large molecular complexes will form by way of association and

solvation, subsequently to persist in a state of kinetic equilibrium,–which will not be inferior in size to the particles existing during the colloid stages of solution and crystallization of substances (vide: Principles 2, 3 and 4).

To the same species of the colloid state the solutions also belong of such solid substances, of which the molecules contain *a large number of atoms condensed by ordinary chemical forces* (e. g. the proteins and the like), or — to put it in a different way — the solutions of substances of composite chemical nature.

All the above enumerated principles hold equally for the case of the coexistence of phases other than solid and liquid[1] (e. g.: liquid and liquid).

B. Principles on the Temperature Irreversible Dispersoid State (the Dispersoid State of Substances Present under the Conditions of Slight Solubility)[2].

I. ON THE DISPERSOID SOLUTIONS OF SMALL CONCENTRATIONS.

On realizing the reaction, which is practically instantaneously completed, of the formation of any substance in a dispersion medium in which this substance is little soluble, there arises a dispersoid solution of this substance, which is sufficiently stable with small concentration of the reacting solutions; however insignificant the solubility of the substance in the dispersion medium selected, and however indifferent this latter might be toward the substance, it is still possible

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1 This I had pointed out in my communications read before the Russian Chemical Society on Dec. 7, 1906, and April 5, 1907, and so on. / Journ. Russ. Chem. Soc. **38**. 1400 (1906); **39**. 619–621 (1907)/. Quite independently from my works, *Wo. Ostwald* arrived in 1907 at his teaching of disperse systems, and gave them a rational classification (Koll.–Zeitschr. **1**. 331–341/ 1907/) /April–May issues/.

2 I confine myself to adducing the principles pertaining to the preparation of dispersoid solutions and dispersoid precipitates of solid substances in liquids by the crystallization method.

to prepare, with sufficiently small (sometimes–insignificantly small) concentration of the reacting solutions, a sufficiently stable dispersoid solution of this substance.

II. ON THE DISPERSOID SOLUTIONS OF CONSIDERABLE CONCENTRATIONS.

1. The dispersoid solutions of considerable concentrations will immediately coagulate in such dispersion media as are practically altogether indifferent toward the disperse phase.

2. For the preparation of dispersoid solutions of considerable concentration, the presence is requisite of conditions for dispergation[1]

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1 *The fundamental conditions for dispergation (peptisation).* The conditions for dispergation are as follows: (Compare e.g. *P. P. von Weimarn.* Journ. Russ. Chem. Soc. **40**. 1785 / 1908 /; Koll.–Zeitschr. **4**. 127 / 1909 /; Grundzuge der Dispersoidchemie. 76 / 1911 /; Kolloidchem. Beih. **1**. 105 / 1910 /; Kolloides und kristalloides Loesen und Niederschlagen. 554–638. Kyoto 1921.)

a). The dispergator, that in the substance which is introduced into the dispersion medium in order to obtain a stable dispersoid solution, must form, when present in sufficiently high concentration, a soluble chemical compound with the disperse phase in question; with small concentration of the dispergator, no such compound must be formed, or else it must be strongly dissociated, so that the disperse phase be also the saturating substance.

b). Previous to the introduction of the dispergator, the dispersion medium must practically not resolve the disperse phase.

If, in preparing a dispersoid solution, one starts from a precipitate, the degree of dispersity of this precipitate must be near to the dispersoidal degree of dispersity.

The experimental material from which these conditions were derived is very extensive: not only had I repeated *A. Lottermoser's* experiments with silver salts in aqueous media, but I have additionally carried out investigations on the peptisation of the precipitates of these salts in mixtures of water and alcohols of the fatty series, as well as of many other salts of the alcaline-earth and the heavy metals, and also of elementary substances (such as: Ag, Au) and hydroxides (e.g. of Fe, Al, Si). Notwithstanding the multifariousness of the substances, the general results obtained were thoroughly equal. Owing to the progressively decreasing capacity of the alcoholic-aqueous media to produce dissociation, it was possible, easily to regulate the processes which are taking place at the surfaces of the dispersed particles; I was thus able to establish that the dispergation ability is directly dependent on the energy with which the soluble chemical compounds arising at corresponding conditions are retained by the dispersion medium; this energy is varying, in most cases, as a first approximation, in the same sense as varies the solubility of the dispergator, and series of dispergators are thus obtained (similar to those by *Hofmeister*), closely connected with the solubility and the solvation capacity.

(peptisation) and for dispersoidal parasitism[1]. If these conditions are present, then any substance can be obtained in the state of extremely stable (for years, decades, and possibly—centuries) dispersoid solutions, of which the concentration may attain—to the detriment of stability, of course—several percent, or even several tens percent.

3. The complex compounds, *which exist for every substance*, make it possible to realize, for any substance, the conditions necessary and sufficient for dispergation (peptisation) and for dispersoidal parasitism, and to prepare stable dispersoid solutions of high concentrations.

For this purpose, it is necessary to select such a dispersion medium and such temperature conditions, which would make easy the regulation of the dissociation of the above complex compounds.

A mixture of water and alcohols of the fatty series offers an especially convenient dispersion medium for preparing dispersoid solutions at the expense of a dissociation of complex compounds, and of the presence of dispersoidal parasitism: elementary substances (e. g. Ag, Au and others), hydroxides (Si, Al, Fe, and others), salts (sulphates, chromates, carbonates, phosphates, arsenates, phosphites, arsenites, tungstates, molybdates, silicates, sulphides, fluorides, chlorides, bromides, iodides, borates, oxalates, tartrates, citrates, and so on) of the alcaline-earth and the heavy metals, can easily be prepared in the state of stable dispersoid solutions in alcoholic–aqueous media[2].

III. ON THE DISPERSOID PRECIPITATES.

1. Any substance whatever can be obtained under the form of

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1 The *dispersoidal parasitism* / Compare e.g. *P.P. von Weimarn.* Kolloidchem. Beih. **IV.** 125; 188 (1912–1913) / consists in increasing the stability of dispersoid solutions by way of a linking together of the particles of the disperse phase with the molecules or, more generally, with the particles of substances which are more soluble or more strongly tied up with the dispersion medium than is the pure disperse phase. This linking together is mostly not of a static, but of a dynamic character.

Whenever the above explained conditions of dispergation are present in the disperse systems, dispersoidal parasitism takes place to a greater or smaller extent.

2 These solutions can be obtained either through condensation, or through dispergation (peptisation) of precipitates.

dispersoid precipitates, whenever the practically instantaneous reaction of its formation is realized in dispersion media, in which the substance in question is extremely slightly soluble. (The precipitation curves for *normal* cases are given in the drawing on p. 7).

2. The less the dispersion medium selected is able to dissolve the substance in question, and of the more this latter is indifferent toward the dispersion medium, the longer will the high degrees of dispersity of the dispersoid precipitates persist.

3. The homochemical and heterochemical cohesion of the dispersion medium and of the substances either " colloidally " or " truly " dissolved therein, with the disperse phase, makes, *under suitable conditions*, the process slower, of union of the disperse particles (e. g. into aggregates, flakes, crystals), and reduces the rate of the recrystallization process.

This cohesion makes for an increase, *under suitable conditions*, of both the stability of colloid solutions of considerable concentrations, as well as the stability of supersaturated true solutions with large absolute supersaturation, e. g. of supersaturated solutions of well–soluble substances in water or in other solvents.

IV. ON THE FORMS AND THE CHEMICAL COMPOSITION[1] OF THE PARTICLES PRESENT IN THE DISPERSOID SOLUTIONS AND IN THE DISPERSOID PRECIPITATES.

(see : Figs. 1—3).

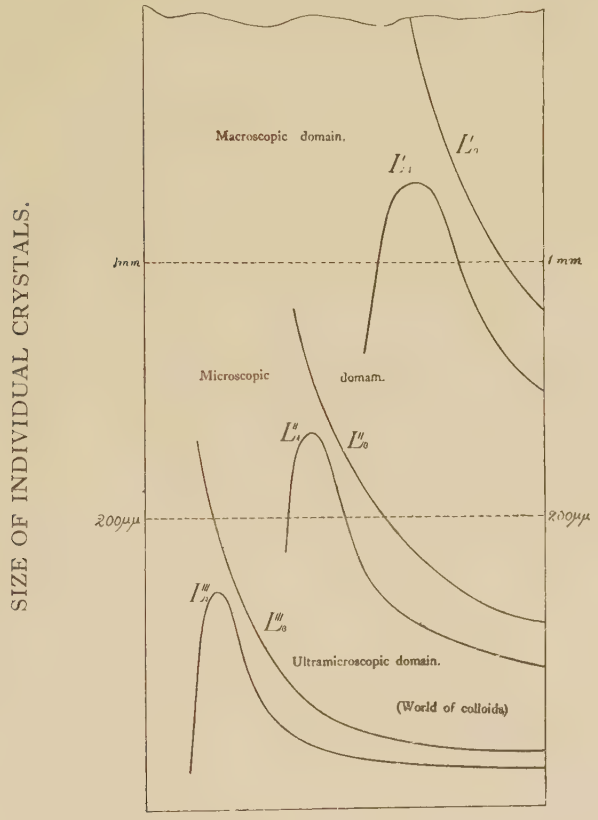
a. On the forms of the particles.

1. The particles in the dispersoid (*suspensoid*) solutions can

[1] *P. P. von Weimarn.* Journ. Russ. Chem. Soc. **39**. " On the Chemical Composition of Microcrystalline and Ultramicrocrystalline Precipitates " 650 (1907) ; " On Indetermined Chemical Compounds " 1461 (1907). News of the St. Petersburg Mining Instit. **1**. 255 (1908) etc.; Koll.–Zeitschr. **2**. 206 (Fig. 3); 327–328 (1908). **6**. 32 (1910). **7**. 156, Fig. 1 (1910); **12**. 308 (1913) and so on; Kolloidchem. Beih. **1**. 399, Fig. 1 (1910); **4**. 88, " Selbstreinigung ' (Selfpurification) 111 and following. Grundzuege der Dispersoidchemie 15–20 (1911). Verlag von *Theodor Steinkopff*. Dreseden, and so on. For a most detailed account, see : *P. P. von Weimarn.* " Kolloides und kristalloides Loesen und Niederschlagen ", Kyoto 1921. Compare : Presentation of this part of my theory of the colloid state in the work by *Leonardo Cassuto*, Der Kolloide Zustand der Materie, 221–222 (Fig. 18), and 230–231 (1913). Verlag von *Theodor Steinkopff*.

Graphic Representation of the Conditions for the Transition of *Any* Solid Substance from the "*World of Crystalloids*" to the "*World of Colloids*" and vice versa under the Influence of the Variations of the Solubility and the Concentration of the Reacting Solutions (respectively the Velocity of Solid Phase Formation).

(In accordance with the theory and the experiments of *P. P. von Weimarn*).



CONCENTRATION OF THE REACTING SOLUTIONS.

(respectively: velocity of solid phase formation).

Explanations:

The precipitation curves (e. g. L_A^I) have, at first, a maximum which, in the course of time, is being displaced to the left and upwards, so that, after the lapse of some time from the beginning of the precipitation, the curves will *practically* assume a sensibly hyperbolic (e. g. L_B^I) form ($y=const./x^n$, where, x, signifies e. g. the absolute supersaturation, being equal to the amount of the substance of which weare studying the precipitation, minus the solubility of this substance: $x=Q-L$).

The solubility L^I is greater than L^{II}, L^{II} being greater than L^{III}. The values of L^{III} are already so small that the substance is said to be under the conditions of a *practically complete* insolubility.

As may clearly be seen from the Scheme, with the decreasing solubility of the substance, *other conditions being equal*, its precipitation curves are shifting downward and extending in the left direction.

What is plotted as ordinates are the magnitudes of the *individual crystals*; one is to be very careful, not to confound them with the magnitudes of the aggregate-particles (aggregates built up of individual crystals) of the precipitates.

either be isolated ultramicrocrystals, or ultramicroaggregates of minute ultramicrocrystals.

2. Dependent on the conditions of dispersoid synthesis, all of the particles present in the dispersoid solution may represent isolated ultramicrocrystals, or all of the particles may be ultramicroaggregates of ultramicrocrystals, or finally, a mixture of both kinds of particles[1] may be present in the dispersoid solution.

3. Dependent on the conditions of dispersoid synthesis, the isolated ultramicrocrystals may represent holohedral crystals, figures of growth, needles (*the long needles are specifically characteristic of such substances as will crystallize in so-called negative crystals*), spherites, and so on.

4. Dependent on the conditions of dispersoid synthesis, and also on the peculiarities of the substance with respect to its crystallization (e. g. its yielding positive or negative crystals), the ultramicroaggregates may either display the form, more or less rounded off (the contours being either somewhat regular or altogether irregular), of ultra microflakes, or they may display the elongated form of ultramicrofibres.

b. On the chemical composition.

1. (See : Fig. 1.). The chemical composition of some substance X which, by the superficial layer of its crystal, is taking up some other substance[2] Y, is expressed by the general formula[3]: XY_{Δ}, where the value of Δ, being practically zero if the substance is taken in coarsely dispersed crystals (e. g. No. 1 in Fig. I), will increase with the increase of the degree of dispersity (respectively-the decrease of the crystal

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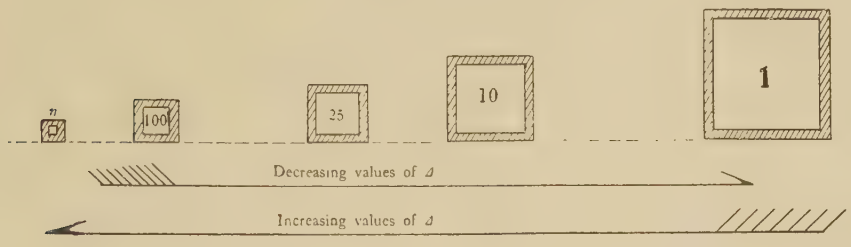
[1] This is the case which is most frequently met with under the ordinary conditions of dispersoid synthesis, whenever not excessively small concentrations of the reacting solutions are used.

[2] This reasoning will certainly not be altered, if some additional substances : Y_1, Y_2, and so on, are taken up simultaneously.

[3] It goes without saying that this is the expression foi the *mean* composition, for it is clear (see Fig. 1) that, while the superficial layer is of some particular chemical composition, the composition of the nucleus of the crystal is a different one (e. g. that of the pure substance X). It is the average of these two compositions that can be expressed by the formula XY_{Δ}

size) and decrease with the decrease of this latter (respectively—the increase of the crystal size).

Fig. 1.

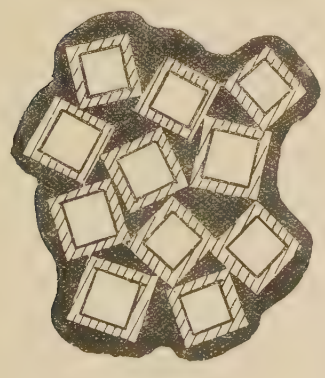


2. In conformity with Principle 1, if the conditions of the experiment are such that the *only* variable is the degree of dispersity (the crystal dimension), then the change in chemical composition of the disperse phase particles is simply a consequence of the magnitude of the surface bound to unit mass having changed.

3. The reasons (see Principle 1) to which the taking up of substance Y by the superficial layer of the crystals X was due may be extremely manifold: they may be of identical nature with those producing true solution of substances (e.g. the formation of complex compounds), but this taking up may also be due to the formation on the surface of the crystals of some insoluble reaction product (e. g. of AgJ on Ag-crystals), and so on.

4. When the size of the ultramicrocrystals becomes *extremely* small (see Fig. 1: the crystals No. 'n', and even smaller ones), so that the superficial layer is already constituting by far the larger part of the ultramicrocrystals, it will no longer be possible to draw a sharp boundary between that kind of ultramicrocrystals and the complex molecular aggregates which are of an equal size with the above ultramicrocrystals (see below: on the vectoriality of the molecules).

Fig. 2.



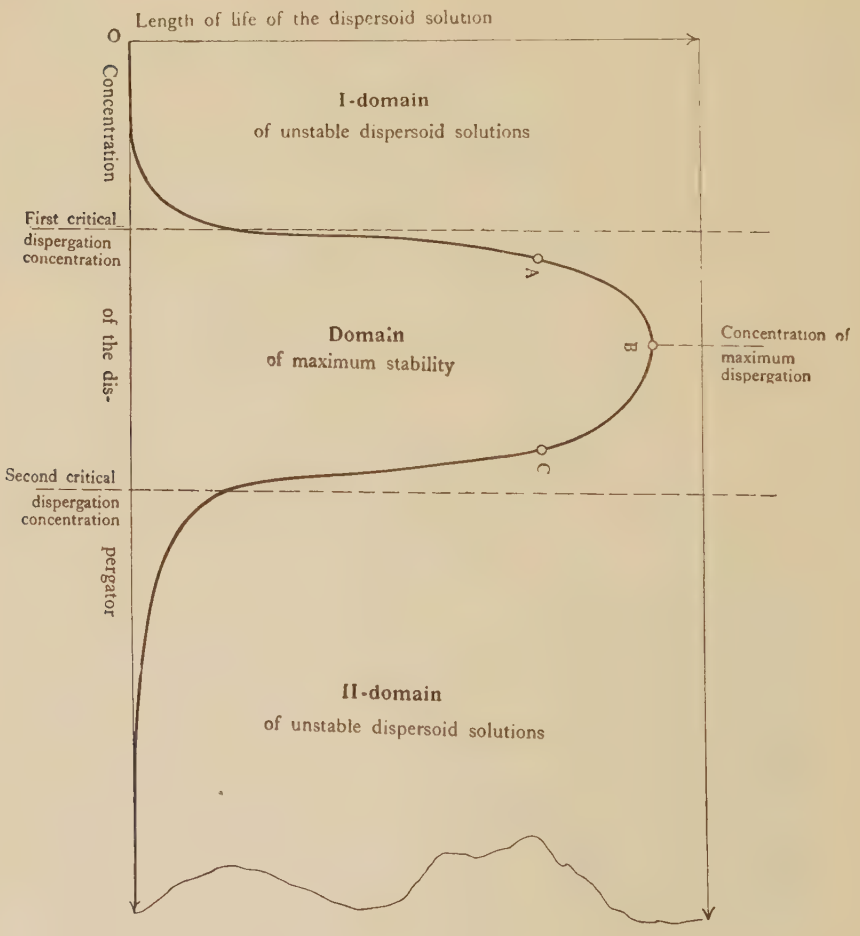
5, (See Fig. 2). The aggregates

of ultramicrocrystals having soaked in into their capillary interstice channels the dispersion medium with everything contained therein, their chemical composition is naturally a still more complicated one than is that of the isolated ultramicrocrystals.

6. With either the contraction or the internal relaxation of the aggregates, a change in chemical composition is taking place.

7. With the breaking down of the aggregates, and with the increase in size of the crystals they were made of, a " self-purification " takes place of disperse phase and of precipitates, while matters absorbed are, of course, given back to the dispersion medium.

Fig. 3.



8. (See : Fig. 3). With varying concentration of the despergator the composition[1] of the dispersed particles ($XD_{\triangle}$) will also vary, keeping pace with the alterations suffered by the dynamic processes which take place at the surfaces of the dispersed particles (both the isolated and the aggregate-particles). For the same length of life (points A and C in the stability curve) the composition of disperse phase in not the same.

9. (See : Fig. 3). It is altogether irrational, to work out theories as to the chemical composition of the disperse phase of dispersoid solutions, on the ground of the results obtained in studying these dispersoid solutions subsequent to their purification, by either dialysis or some other analogous means, for it is quite clear that, by removing the dispergator, we are producing changes in both the composition of the disperse phase and the length of life of the dispersoid solution.

10. (See : Figs. 1, 2 and 3). The dispersoid solutions contain generally, for each given moment, a disperse phase with particles of different magnitudes, these magnitudes (as well as the closeness of contiguity of the ultramicrocrystals within the aggregates) being subject to constant changes in the course of time.

Hence it clearly follows that it is quite out of question, to speak of a *definite* chemical composition of disperse phase.

11. The dispersoid precipitates, which are separated out on coagulation of a dispersoid solution, will go over, with time, into more coarsely-dispersed ones (coarse microcrystals), while acquiring a constancy of composition, for there is a " self-purification " taking place simultaneously, so that in the last item we shall practically have :

$$XY_{\triangle}=XY_0=X.$$

12. The equation :

$$\lim\ (XY_{\triangle})_{t=T}=XY_0=X$$

may be regarded as schematic expression for the limit to the changes in chemical composition of the disperse phase--at first in the dispersoid solution, and afterwards under the form of the precipitate given birth to by the above dispersoid solution—when, after the lapse of time t=T, this disperse phase will have reached a coarsely-disperse (coarsely-microcrystalline) condition.

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1 The letter ' D ' is here to signify symbolically the chemical composition of a *solvated* molecule of the dispergator.

C. Principles on the Temperature-Reversible Dispersoid State.

1. Any substance whatever can be obtained, on cooling its solution sufficiently rapidly, in the state of a highly-disperse jelly or in that of a highly-disperse glass which, on being sufficiently rapidly heated, will, in a reversible way, go over into the original true or dispersoid solution, without separating the substance in a coarsely-disperse condition.

2. In the above processes, the rate of cooling, and the rate of heating can be reduced, by properly selecting the dispersion medium, to values so small, that it becomes *practically* impossible to obtain from such a dispersion medium, the substance in coarsely-disperse condition.

3. The most important factors which permit to obtain any substance whatever in a typical reversible dispersoid condition are: solvation, solventolysis, dispersoidal parasitism, and the ability of the dispersion medium to solidify to glass or to jelly (For instance, the alcoholic-aqueous dispersoid solutions mentioned in Section B, II, 3 are able to solidify reversibly, *under suitable conditions*, so as to form jellies or glasses).

D. The Principle of Vectoriality of Matter.

1. Matter is *vectorial* in all its states; and no such thing as *absolute* amorphy[1] exists in Nature.

This principle is to be understood in the broadest thinkable sense; that is to say, in the sense that, not only are the various *solid* systems which up to the present were and still are described as "amorphous" (e.g. the amorphous and the colloidal precipitates, the glasses, and other formations of a similar kind) made up of very minute particles endowed with *vectorial* structure and *vectorial* forces (i.e. of very minute crystals), but also the particles (molecular complexes, molecules, atoms) as are present in "true" solutions, as well as those

[1] *P. P. von Weimarn.* Journ. Russ. Chem. Soc. 1906 and 1907; Kolloid-Zeitschrift **2**, 83 (1907); 219 (1908) and so on.

constituting the liquids and the gases, are endowed with *vectorial* forces and a *vectorial* structure.

In other words, *vectoriality is a property inherent in matter;* and therefore, whatever the elements into which we might differentiate matter (electrons, subelectrons, and so on), these elements must equally possess *vectorial* forces, and be constructed *vectorially*.

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Note: From September 1907 the publications of the present author began to appear regularly in "Kolloid–Zeitschrift" (respectively in "Kolloidchemische Beihefte") *where they may easily be found.*

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BaSO_4. x**Ba**Cl_2 ; **Ba**SO_4. x**Ba**Br_2 ;.....; **Ba**SO_4. x**Ba**$(NO_3)_2$; ....; **Ba**SO_4. x**Ba**$(CNS)_2$.....; Ba**SO**$_4$. xMn**SO**$_4$; Ba**SO**$_4$. xCo**SO**$_4$; ....; Ba**SO**$_4$. xNa_2**SO**$_4$;.... and so on. Compare also : Koll.–Zeitschr. **32**. 145 (1923).

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